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Effect of promoters in Co–Mn–Al mixed oxide catalyst on N_2O decomposition

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ABSTRACT

Catalytic decomposition of N_2O over calcined Co–Mn–Al layered double hydroxide (LDH) modified with slight amount of alkali (Li, Na, K), rare earth (La, Ce), or noble metals (Pd, Pt) was studied. Two methods of promoter addition were applied: impregnation of LDH-related Co–Mn–Al mixed oxide by a promoter-containing solution and incorporation of the promoter during coprecipitation of the LDH precursor. The method of preparation affected the reducibility of the obtained mixed oxide catalysts but its effect on the surface area (with the exception of a cerium-contained sample) and N_2O conversion was less evident. The modification of the Co–Mn–Al mixed oxide with K or Na increased N_2O conversion, while no effect or a decrease in the N_2O conversion was observed over the other examined catalysts. Alkali metals act as electron promoters; therefore, the differences in catalytic activity may be related to changes of oxygen-transition metal bond strength. The Co–Mn–Al mixed oxides with 1.8 wt% K exhibited a high catalytic activity even under the simultaneous presence of O_2, H_2O and NO_x. The laboratory stability test revealed maintenance of the beneficial effect for 360 h.

1. Introduction

Nitrous oxide is known as a strong greenhouse gas and also as the gas depleting the ozone layer. Nitrous oxide decomposition according to Eq. (1) represents the easy abatement process for N_2O emissions reduction. This reaction is the spin-forbidden reaction with high activation energy (250–270 kJ/mol) and a measurable N_2O conversion is obtained only above 627 °C [1]:

$$2N_2O \rightarrow 2N_2 + O_2 \qquad (1)$$

However, a complete N_2O conversion can be achieved at much lower temperatures in the presence of a catalyst, depending on the catalyst used and the composition of the inlet gas.

Decomposition of nitrous oxide can be applied for abatement of the N_2O emissions in waste gases, e.g., from nitric acid plants, which have been indicated as the greatest industrial source of anthropogenic N_2O emissions (worldwide 400 kt N_2O per year) [2]. Several positions are possible for N_2O abatement: (i) high-temperature homogeneous decomposition of N_2O downstream of the ammonia burner [3,4], (ii) high-temperature catalytic decomposition situated immediately downstream of the ammonia burner [5–7] and low-temperature catalytic N_2O decomposition upstream or downstream of the tail-gas expander and the NO_x emissions reduction technology ($DeNO_x$) [8–10]. While homogeneous N_2O decomposition requires a new design of the ammonia oxidation unit, catalytic decomposition is a cost-efficient process option easily applicable in any existing plant. Therefore, the catalytic N_2O decomposition has been intensively studied by many academic institutes and research teams. Regardless, it is still a problem to find a catalyst with sufficient activity and stability in real off-gas conditions because of water, oxygen and NO_x inhibition effect [1].

In this study, we decided to concentrate on low-temperature (≤450 °C) catalytic N_2O decomposition. Many different catalysts have been studied in the process during the last two decades [1], especially Fe-zeolites [11–14], noble metals (Rh, Ru, Pd) on various supports [15–17], Cu- [18,19], Co-containing catalysts [20,21] and mixed oxides prepared from layered double hydroxides (LDHs) precursors [22–26]. The mixed oxides prepared by thermal treatment of LDHs offered favorable results in the N_2O catalytic decomposition.

Layered double hydroxides (known also as hydrotalcite-like compounds or anionic clays) 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 the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{n-}_{x/n} \cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n-} is an n-valent anion, and x usually has values between 0.25 and 0.33. After heating at moderate temperatures LDHs give finely dispersed mixed oxides of M^{II} and M^{III} metals with sufficiently high surface area and reasonable ther-

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Table 1
Physical–chemical properties of Co–Mn–Al mixed oxide modified with promoters.

Sample	Promoter content (wt%)	S_{BET} (m^2/g)	TPR H_2 (mmol/g) 25–800 °C	T_{max} (TPR)[a] (°C)	TPD-CO_2 ($mmol/m^2$) 25–500 °C	TPD-NH_3 ($mmol/m^2$) 25–500 °C	N_2O conversion[b] X(360) (%)
Non-modified	0	93	11.38	352; 731	0.57	3.37	18
0.1% Pd*	0.10	100	12.63	350; 727	1.29	3.53	17
0.1% Pt*	0.08	92	11.89	338; 492	1.07	5.61	14
0.4% La*	0.42	93	11.77	372; 751	0.83	3.37	16
2.8% La*	2.78	93	11.94	391; 756	1.23	3.27	13
0.4% Ce*	0.43	96	12.33	377; 756	0.66	1.94	18
3.0% Ce*	3.01	60	10.88	387; 768	2.28	8.57	12
0.1% Li*	0.10	n.d.	12.18	332; 689	n.d.	n.d.	10
0.3% Li*	0.26	100	10.66	370; 720	1.38	1.51	6
1.5% Li*	1.49	80	13.25	372; 636	0.89	n.d.	0
1.4% Na*	1.39	91	11.10	372; 651; 672	1.65	2.49	35
0.5% K*	0.47	103	11.54	376; 768	1.14	1.60	23
2.5% K*	2.50	86	11.84	286; 352; 725	1.60	2.91	68
0.1% Pd	0.09	101	11.36	252; 470	0.76	3.81	17
0.1% Pt	0.09	81	11.98	332; 453	1.48	3.07	15
0.5% La	0.47	96	10.37	354; 739	1.24	4.93	22
2.8% La	2.84	96	10.19	368; 729	1.04	3.98	9
0.6% K	0.60	111	11.15	364; 706	0.98	2.83	21
1.8% K	1.76	98	11.16	296; 350; 702	1.19	2.89	72

[a] Maxima of reduction peaks determined from TPR (H_2) measurements.

[b] 0.1 mol% N_2O in He, SV = 60 l g^{-1} h^{-1}.

mal stability. The cation composition of LDH-related mixed oxide catalysts can be simply adjusted during precursor synthesis; a coprecipitation of aqueous solutions containing M^{II} and M^{III} cations in adequate proportions with an alkaline solution is mostly applied [27].

The Co–Mn–Al mixed oxides with Co:Mn:Al molar ratio of 4:1:1 have been found to be the most active catalysts for N_2O decomposition among all LDH-related catalysts tested by our group [28]. Our effort to increase further catalytic activity of the mentioned catalyst led us to the study of the effect of low amounts of promoter incorporation into the catalyst. In chemical literature we found that some noble metals (Pt, Rh, Pd, Ru) [29,30], alkali metals (Li, Na, K, Rb, Cs) [31–34] and other (La, Ce, Ba) [35,36] were tested as catalyst promoters for N_2O decomposition.

Alkali metals can substantially affect the properties of oxide catalysts, because they act, in consequence of their exceptionally low ionization potentials, as electronic and structural promoters, modifying the acid–base function of the surface, and due to their relatively large dimensions, possibly behave as site blocking species [37].

In the present work, we modified the parent Co–Mn–Al mixed oxide with small amounts of alkali (Li, Na, K), rare earths (Ce, La) or noble metals (Pt, Pd) in order to improve its activity for N_2O decomposition. Two methods of promoter addition into the Co–Mn–Al mixed oxide were applied (impregnation of the mixed oxide and introducing of the promoters in the stage of LDH coprecipitation). The objective of the presented work is the finding of active and stable catalysts for low-temperature N_2O catalytic decomposition in conditions of waste gas from HNO_3 plant, and examination of the effect of the promoters added by two different ways on the catalytic and physical–chemical properties.

2. Experimental

2.1. Catalysts 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 Na_2CO_3/NaOH solution at 25 °C and pH 10. The washed and dried product was calcined for 4 h at 500 °C in air. The prepared mixed oxide was then crushed and sieved to obtain a fraction with particle size of 0.160–0.315 mm, which was used for catalytic measurements. This catalyst was examined as a reference sample and was labeled as a "non-modified" sample. Samples modified with promoters were prepared by two methods:

(i) The "non-modified" mixed oxide catalyst was impregnated by the pore filling method in solutions containing the promoter (aqueous solutions of $Pd(NO_3)_2$, $Pt(NH_3)_4(NO_3)_2$, $La(NO_3)_3{\cdot}6H_2O$, $LiNO_3$, $NaNO_3$ and KNO_3). After drying at 105 °C, the impregnated samples were again calcined and sieved at the same conditions as mentioned above. Samples were labeled according to their promoter content, e.g., 0.5% La* means Co–Mn–Al mixed oxide catalyst modified by 0.5 wt% of lanthanum, when the impregnation procedure was applied. (ii) The soluble promoter-containing compounds ($PdCl_2$, H_2PtCl_6, $La(NO_3)_3{\cdot}6H_2O$) were added into the nitrate solution used for coprecipitation of LDH precursors or to the washed precipitate (modification by K when an aqueous solution of KNO_3 was applied). The dried products were calcined for 4 h at 500 °C in air and sieved to obtain a fraction with particle size of 0.160–0.315 mm. Catalysts were labeled according to their promoter content but without the asterisk. For example, the 0.5% La sample denotes the Co–Mn–Al mixed oxide catalyst modified by 0.5 wt% of lanthanum in the stage of preparation of the LDH precursor.

The catalysts were characterized by several methods—atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES), adsorption/desorption of nitrogen at −196 °C, temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) of pre-adsorbed NH_3 or CO_2 and TPD-O_2 in inert gas. The details of used methods are described in electronic Supplementary material.

2.2. Catalytic measurements

Catalytic measurements of N_2O decomposition were performed in an integral fixed bed stainless steel reactor of 5 mm internal diameter in the temperature range of 300–450 °C and under atmospheric pressure. Total flow rate was kept at 100 or 300 ml min^{-1} (NTP). The catalyst bed contained 0.1 or 0.3 g of sample with particle size 0.160–0.315 mm. The space velocity (SV) of 20 or 60 l g^{-1} h^{-1} was applied. Feed to the reactor contained 0.1 mol% N_2O; oxygen (5 mol%), NO (0.005–0.17 mol%), NO_2 (0.17 mol%) and water vapor (0.9–4 mol%) were added to some catalytic runs. The reactor was heated by a temperature-controlled furnace. Before each run, the catalyst was pre-treated by heating it in a He flow (100 ml min^{-1}) at 450 °C and maintaining this temperature for 1 h. Then the catalyst was cooled to the reaction temperature and the steady state of the N_2O concentration level was measured. The used analytical equipments are described in electronic Supplementary material.

The rate constants were determined according to the 1st order rate law $(-r_{N_2O}) = k\,p_{N_2O}$. To evaluate the kinetic data, conversions less than 50% were taken into account only. The activation energies and pre-exponential factors were evaluated from Arrhenius plot and then, rate constant k at temperature of 400 °C was extrapolated using Arrhenius equation.

3. Results and discussion

3.1. Characterization of the catalysts

The physical–chemical properties of the prepared catalysts are summarized in Table 1. The content of promoters determined by chemical analysis differed only slightly from the expected values adjusted during preparation of the catalysts. In addition, a small amount of Na (less than 0.11 wt%) was present in all samples; this residual Na was not completely washed from the product after coprecipitation of the LDH precursors. Sodium can also act as a promoter for N_2O decomposition but its effect is supposed to be negligible in this particular case with low Na content.

A well-crystallized hydrotalcite-like phase with a slight amount of $MnCO_3$ (rhodochrosite) admixture was found in the powder XRD patterns of the prepared LDH precursors; the addition of promoters during precursor preparation did not affect the phase composition of the obtained products (not shown here). In the powder XRD patterns of the prepared catalysts, the Co–Mn–Al mixed oxide with spinel structure was found as it was reported formerly [38,39]. Spinel-type oxides are the primary crystallization products during thermal treatment of the cobalt-containing LDHs; a segregation of Co-enriched spinels of Co_3O_4 type with a gradual incorporation of Mn and Al into the spinel lattice at moderate calcination temperatures can be expected in the Co–Mn–Al systems [39]. Beyond the spinel, no other phases were detected in the Co–Mn–Al catalysts modified with promoters. The exception was a trace amount of a birnessite-type oxide, K_xMnO_2, detected in the LDH-related Co–Mn–Al mixed oxides modified with a higher amount of potassium [40]. Small Li cations diffused into the spinel lattice and caused a slight decrease in the lattice parameter of the Co–Mn–Al spinel. The following lattice parameters of the spinel-type Co–Mn–Al mixed oxide were evaluated from the powder XRD data (in Å): 8.116, 8.105, 8.107, and 8.087 for the non-modified, 0.1% Li*, 0.3% Li*, and 1.5% Li* samples, respectively; the error of 0.002 Å in the evaluated lattice parameters was estimated. No marked changes in the spinel lattice parameter were observed after modification of the parent Co–Mn–Al mixed oxide with other promoters.

The surface areas of the prepared catalysts ranged from 80 to 111 m^2 g^{-1}; a lower value of 60 m^2 g^{-1} was found only with the 3.0% Ce* sample (Table 1).

TPR results measured in the temperature range from 25 to 900 °C are also summarized in Table 1. As expected, the H_2 consumption was nearly the same for all catalysts due to a low content of promoters. In contrast, differences in reducibility of the modified catalysts were found in the measured TPR patterns (Figs. 1 and 2). The parent (non-modified) Co–Mn–Al catalyst was reduced in two main temperature regions. Both reduction peaks consist of overlapping peaks corresponding to the co-effect of more species. According to the former reports [28,41,42] the low-temperature peak (200–400 °C) consists of two peaks representing the reduction of Co^{III} to Co^{II} and Co^{II} to Co^0. The reduction of Mn^{IV} species also cannot be omitted in this temperature interval. The high-temperature peak (400–900 °C) is attributed to the reduction of Co and Mn cations surrounded by Al ones in a spinel-like phase.

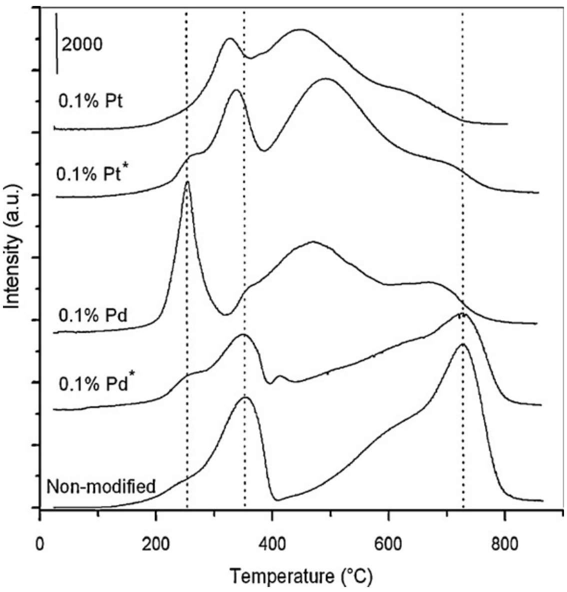

Fig. 1. TPR patterns of the Co–Mn–Al mixed oxide modified with various amounts of platinum and palladium; promoter was added during coprecipitation of LDH precursor (0.1% Pt, 0.1% Pd) or during impregnation of the LDH-related mixed oxide (0.1% Pt*, 0.1% Pd*).

Incorporation of a small amount of noble metals (Pd and Pt) had a significant effect on the reduction properties of the modified Co–Mn–Al catalysts (Fig. 1). In the case of 0.1% Pt, and 0.1% Pt* catalysts, a marked shift of the high-temperature peak to lower temperatures was observed, agreeing for both catalysts but more distinct for the coprecipitated catalyst. Obviously, platinum makes reduction of Co and Mn spinel-like phase easier. Dispersion of Pt in the coprecipitated catalyst is evidently better than in case of

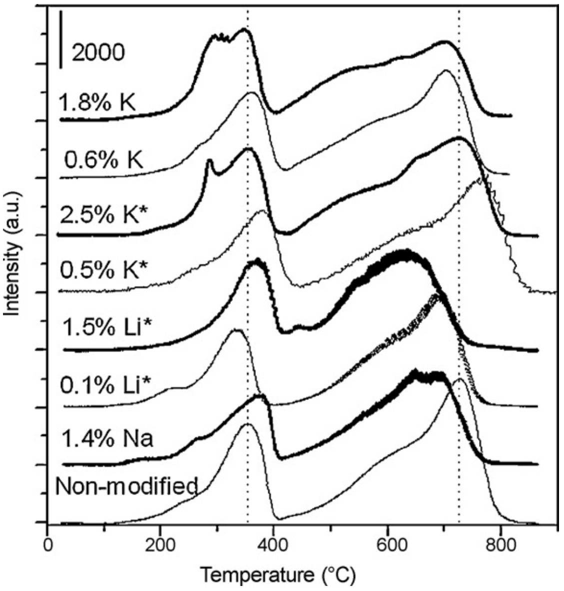

Fig. 2. TPR patterns of the Co–Mn–Al mixed oxide modified with various amounts of alkali metals; promoter was added during impregnation of LDH-related mixed oxide (samples labeled as *) or after coprecipitation of LDH precursor (0.6% K, 1.8% K).

the impregnated catalyst and for that reason its effect is more pronounced.

On the other hand, presence of palladium in Co–Mn–Al manifested itself differently from platinum during the catalyst reduction. The 0.1% Pd* catalyst prepared by impregnation showed nearly identical course of the TPR pattern in both the low- and high-temperature region as that of the non-modified catalyst. Very likely, impregnation of a parent catalyst with a solution of $Pd(NO_3)_2$ led to the formation of big Pd particles, not in a close contact with other metal oxides. On the contrary, the 0.1% Pd catalyst prepared by coprecipitation showed quite different course of reduction. A sharp low-temperature peak at about 252 °C was appeared, and a high-temperature peak was shifted to the temperature range of 600–750 °C, similarly as that one found with the modified 0.1 Pt* catalyst. Obviously, incorporation of Pd into the LDH-like compound led to the formation of small Pd particles making reduction of Co and Mn oxides easier.

Addition of Ce or La did not cause substantial change in the shape of the reduction peaks observed in the TPR patterns. TPR patterns of the Ce-, as well as La-containing catalyst (not shown here) were very similar, but, with increasing Ce or La content in the impregnated catalysts, the reduction maxima in both main reduction peaks were shifted to higher temperatures, which indicated a worse reducibility of both catalysts.

TPR patterns of the Co–Mn–Al catalysts modified with alkali metals are compared in Fig. 2. The samples with low K content (0.5% K* and 0.6% K) exhibited a slight shift of the low-temperature reduction maxima to higher temperatures (the shift was more apparent in the case of 0.5% K* sample) and the peaks had similar shape like the non-modified catalyst.

In the TPR patterns of the samples with higher K content (1.8% K and 2.5% K*), a new reduction peak was clearly visible in the low-temperature region, though some indication of its presence can be found in other samples as well. The same new reduction peak in TPR patterns of the calcined Co-Al LDH modified with K was observed by Cheng et al. [34]. A reason for the presence of this peak in TPR patterns of K-containing Co–Mn–Al mixed oxide has been already discussed in our recent reports [40,43].

The addition of other alkali metals (Na, Li) caused a shift of low-temperature reduction peak to somewhat higher temperatures for all catalysts except the 0.1% Li* and, at the same time, a shift of the high-temperature reduction peak to somewhat lower temperatures. The shifts of reduction maxima to lower temperatures indicated a better reducibility of the catalysts and a decreasing strength of the oxygen-metal bond. No significant changes in the shape of reduction peaks were found except a broadening of the high-temperature reduction peak observed in TPR patterns of the 1.4% Na* and 1.5% Li* samples.

The course of TPD-NH_3 gives information on the amount and strength of acidic sites. The amount of the acid sites is given by the amount of ammonia desorbed in the chosen temperature range and their strength is related to the corresponding desorption temperature. Generally, the acid sites are classified into the weak (<200 °C), medium (200–350 °C) and strong (>350 °C) acid sites. The TPD-NH_3 patterns of the alkali modified Co–Mn–Al catalysts can be seen in Fig. 3. Number of acidic sites in the catalysts calculated per 1 m^2 showed similar order as the amount of acidic sites related to 1 g of catalyst because the catalysts surface areas did not differ too much. The patterns prove the presence of the weak and medium acid sites in all catalysts, the highest amount being found for the catalysts modified with Pt, Ce and La (Table 1) and the lowest one for the catalysts modified with K and Li. It is necessary to note that not all ammonia was desorbed from the catalysts in the temperature range 25–500 °C. It was found out during separate TPD-NH_3 experiments performed using a mass spectrometer that about 15% of ammonia is desorbed at temperatures higher than 500 °C (maximum at 675 °C). Nevertheless, the ammonia amount strongly bonded to these acidic sites cannot participate in any way in the catalytic reaction.

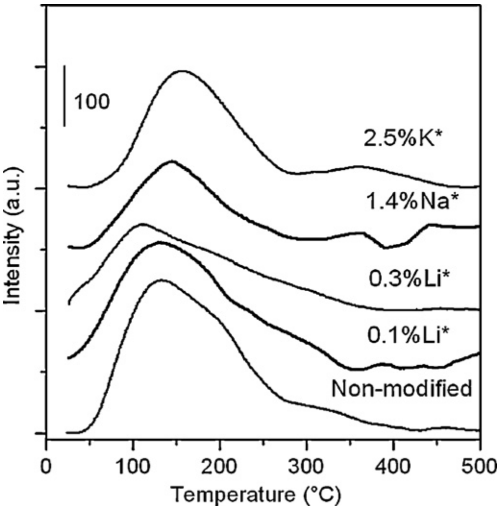

Fig. 3. TPD-NH_3 patterns of the Co–Mn–Al mixed oxide modified with various amounts of alkali metals; promoter was added during impregnation of LDH-related mixed oxide.

Similarly as the acidic properties, also basic properties of the catalysts can be determined from the temperature-programmed desorption experiments using CO_2 as a sorbate. Example of the observed TPD-CO_2 patterns of alkali modified catalysts can be seen in Fig. 4. The TPD-CO_2 pattern of the non-modified catalyst shows two distinct peaks with maxima around 100 and 190 °C proved the presence of the weak and medium basic sites in the catalyst. Analogous courses of the TPD patterns were observed with the 2.5% K* and 0.1% Li* catalysts, whereas addition of Na (1.4%) and higher amount of Li (0.3%) evolved formation of stronger basic sites, from which CO_2 was desorbed at higher temperatures. There is an indication of increasing CO_2 desorption at temperature around 500 °C in the patterns that can be caused by CO_2 coming from the rest of carbonates remaining in the calcined catalysts from the non-thoroughly decomposed carbonates during calcination. The amounts of basic sites calculated per 1 m^2 for the catalysts are shown in Table 1. The highest number of the sites was found for the catalysts modified with the 3% Ce*, 2.5% K* and 1.4% Na* catalysts, whereas the lowest one with the non-modified catalyst, 0.4%

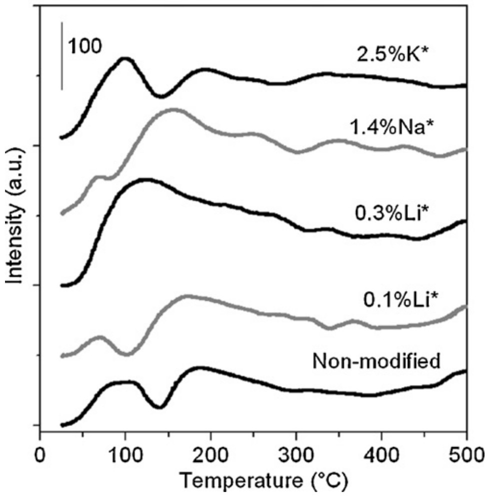

Fig. 4. TPD-CO_2 patterns of the Co–Mn–Al mixed oxide modified with various amounts of alkali metals; promoter was added during impregnation of LDH-related mixed oxide.

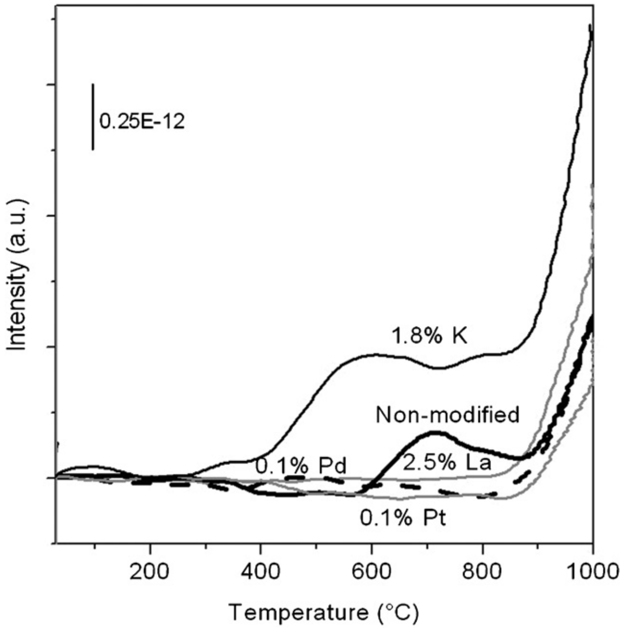

Fig. 5. TPD-O_2 patterns in inert gas of the Co–Mn–Al mixed oxides modified with various amounts of promoters.

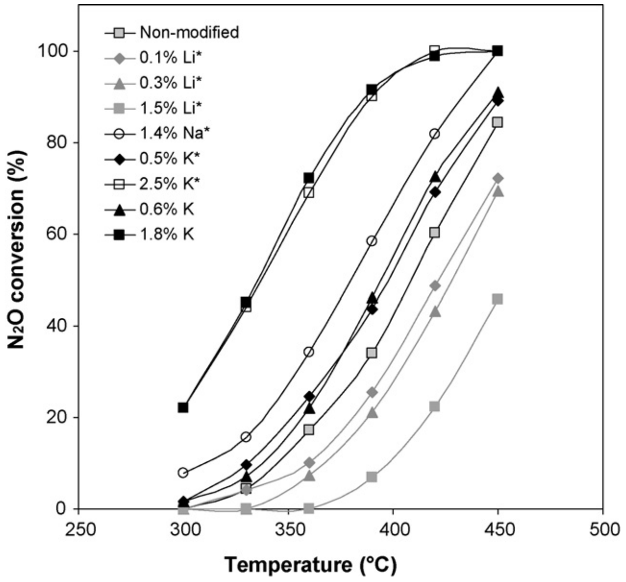

Fig. 6. Temperature dependence of N_2O conversion over Co–Mn–Al mixed oxide catalysts modified with alkali metals (Li, Na, or K); promoters were added after coprecipitation of LDH precursor (0.6% K, 1.8% K) or during impregnation of LDH-related mixed oxide (samples labeled as *). Conditions: 0.1 mol% N_2O in He, SV = 60 l g^{-1} h^{-1}.

Ce* and 0.1% Pd. From the data shown in Table 1 can be seen that surface of the catalysts contains 2–5 times higher number of acidic sites than the basic. Comparing the obtained acid–base data it is obvious that an increase in surface acidity evolved by promoters decreases basic properties of the catalysts.

In order to compare the oxygen mobility in catalyst lattice, especially in subsurface region, chosen catalysts were studied for the temperature-programmed desorption of O_2 from the fresh catalysts to the inert gas (Fig. 5). The non-modified Co–Mn–Al mixed oxide shows the desorption peak of O_2 with maximum at temperature of 720 °C, modification by K caused a substantial shift of this maximum to lower temperatures (by 250 °C). In contrast to it, no oxygen desorption was observed from the catalysts modified by Pd, Pt and La indicating that these promoters decrease oxygen mobility in Co–Mn–Al mixed oxide.

3.2. N_2O catalytic decomposition in inert gas

The temperature dependencies of N_2O conversions are shown in Fig. S1 (see the Supplementary material) and Fig. 6. Modification of the Co–Mn–Al mixed oxide catalyst with Pd, Pt, La or Ce caused minor changes in its catalytic activity (Fig. S1), while substantial differences in N_2O conversion were observed over the catalysts modified with alkali metals (Fig. 6). Nearly the same N_2O conversions were reached over the catalysts modified by the same amount of promoters but prepared by different methods (Table 1).

The catalytic measurements showed only a negligible decrease in the activity of samples containing a higher amount of La (2.8% La*, 2.8% La) and Ce (3.0% Ce*) in comparison with the non-modified sample (Fig. S1). The N_2O conversion over the catalysts containing Pd, Pt and a low amount of Ce were almost the same. In contrast, Tzitzios and Georgakilas [44] reported that a small amount of Pd had a positive influence on the N_2O conversion while a higher content of Pd caused a decrease of catalytic activity. The effect of the promoter amount on the catalyst activity was observed for La-containing Co–Mn–Al catalysts when La was added during coprecipitation of the LDH precursor. Compared to the non-modified catalyst, the 0.5% La sample showed an imperceptibly higher activity in N_2O conversion, whereas the 2.8% La sample showed a lower activity. The Pd-containing samples were slightly more active than the Pt-modified ones; these results are consistent with the findings reported by Doi et al. [45]. Compared to the non-modified catalyst, the presence of 3 wt% Ce in the Co–Mn–Al oxide caused a decrease in N_2O conversion. A similar result was reported by Chang et al. [25]: the N_2O conversion decreased with increasing Ce content in the catalyst, as cerium exhibits an oxygen accumulation tendency, which negatively influences the N_2O decomposition.

The catalysts modified with K and Na showed a higher catalytic activity in comparison with the non-modified one. In opposite, the activity of the catalysts modified with Li was lower and decreased with increasing Li content (Fig. 6). Effect of the Li promoter was completely different from the findings in [33], where the presence of the Li promoter in Co_3O_4 had a positive effect. On the contrary, Cheng et al. [34] obtained the same results as we did: the presence of Li in Co–Al mixed oxide caused a decrease of N_2O conversion. The possible reason could be the different Li-containing salt used for impregnation: $LiNO_3$ was used by Cheng in this work, while Stelmachowski et al. used Li_2CO_3 [33].

Different dependence of N_2O conversion on the K content than in the case of Li was observed for K-promoted catalysts. Fig. S2 (see the Supplementary material) shows the results of N_2O catalytic decomposition over K-promoted Co–Mn–Al mixed oxide from our previous work [43] and from this study. It is visible that N_2O conversion increased with increasing K content up to 1.1–2.5 wt% K (0.028–0.064 mol K/100 g); the further increase of K content in the catalyst caused a decrease of N_2O conversion.

For comparison of the effect of all tested promoters, the N_2O conversions were plotted against content of promoter expressed as a mole of metal in the same amount of catalyst (Fig. 7). Li and higher amount of La and Ce caused decrease of N_2O conversion. The positive effect of K was higher than the effect of the same molar content of Na.

The apparent activation energy and rate constants at 400 °C were derived to evaluate the intrinsic activity of alkali promoted Co–Mn–Al mixed oxide assuming the first order kinetics of N_2O catalytic decomposition [46]. The values of kinetic parameters are

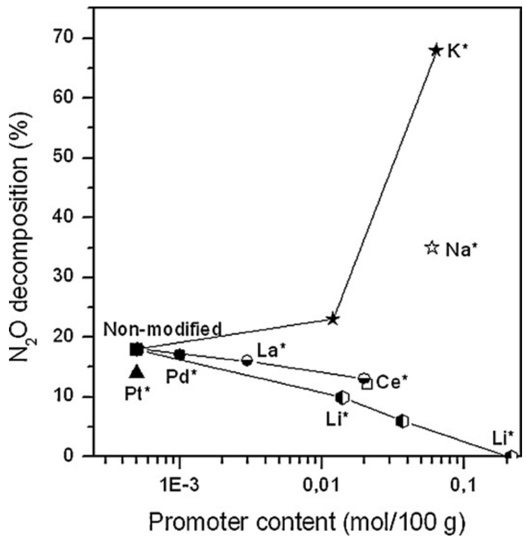

Fig. 7. Dependence of N_2O conversion on promoter content in Co–Mn–Al mixed oxide catalysts. Conditions: temperature 360 °C, 0.1 mol% N_2O in He, SV = 60 l g^{-1} h^{-1}.

summarized in Table S1 (see the Supplementary material). Values of kinetic constants agree well with trend shown in Figs. 6 and 7 indicating that specific surface area is not the decisive parameter for catalysts activity. The order of apparent activation energy is different due to compensation effect. Comparing samples with nearly the same content of Li, Na and K expressed as a mole of metal in the same amount of catalyst (0.3% Li*, 1.4% Na* and 1.8% K or 2.5% K*), the sequence of the promotional effect of alkali on N_2O decomposition – revealed by the increase in rate constants – is: Li < non-modified < Na < K.

It is generally accepted that N_2O catalytic decomposition proceeds by a redox mechanism. The N_2O chemisorption accompanied by charge transfer to the N_2O antibonding orbital and desorption of nascent oxygen accompanied by charge transfer back to the active site constitute a catalytic cycle [1]. Since oxygen desorption is generally considered as the slowest step, the mobility of surface and subsurface oxygen can increase the reaction rate of N_2O decomposition [23]. Mobility of oxygen was studied by TPD-O_2 and the obtained results agree well with the statement mentioned above: in temperature region when N_2O catalytic decomposition was studied (≤450 °C), presence of K in catalysts caused substantial oxygen release. Such release was not observed over other examined catalyst (non-modified, 0.1% Pd, 2.5% La and 0.1% Pt) showing nearly the same catalytic activity (Fig. 5).

Previously reported papers [33,47] imply that the effect of alkali promoters on N_2O catalytic decomposition can be caused by a modification of electronic properties of the catalyst surface gauged by the catalyst work function facilitating redox processes that occur between the catalyst surface and the reaction intermediates produced during the N_2O decomposition. The extent of the catalyst work function changes caused by different alkali metals is dependent on produced surface dipole moments which are influenced by different ionic radius, electronegativities of alkali adcations and their coverage on the surface [33]. Modifications of electronic properties also reflect in changes of metal–oxygen bond strength as was clearly visible from the TPR patterns of alkali modified Co–Mn–Al mixed oxide.

Based on the observed changes in the lattice parameter of the Co–Mn–Al spinel, diffusion of small Li cations into the spinel lattice is proposed. On the other hand, a diffusion of the bigger Na and K cations into the spinel lattice is much more difficult and they are probably accumulated on the catalyst surface as was indicated from XPS analysis of K-promoted Co–Mn–Al mixed oxide [43].

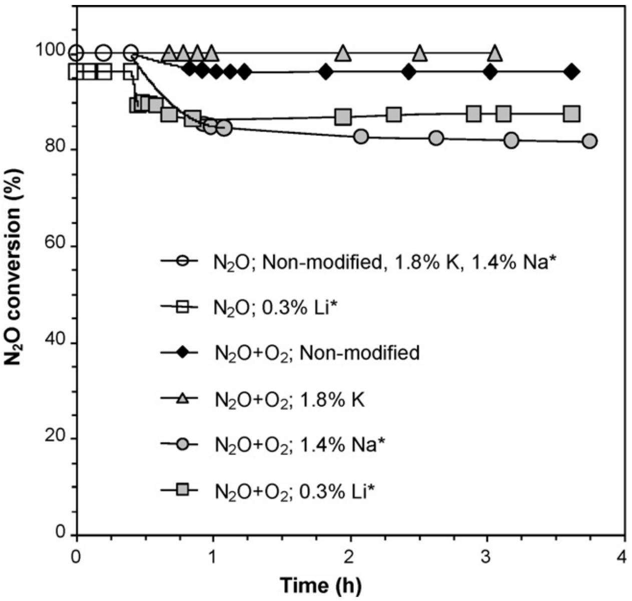

Fig. 8. Influence of O_2 on the N_2O conversion over alkali promoted Co–Mn–Al mixed oxides. Conditions: temperature 450 °C, 0.1 mol% N_2O in He, 5 % O_2, SV = 20 l g^{-1} h^{-1}.

3.3. *N_2O catalytic decomposition in the presence of O_2, H_2O, and NO_x and catalysts stability*

Potential catalyst's application for the abatement of N_2O emissions from nitric acid production evolves necessity of studying the effect of other actual gases (O_2, H_2O, NO, and NO_2) on the catalyst's activity and stability.

The effect of oxygen on the activity of Co–Mn–Al mixed oxide modified by the same alkali metal's molar content is shown in Fig. 8. It can be seen that no oxygen influence was observed on the most active 1.8% K catalyst. In the other cases, the decrease of N_2O conversion was observed. The highest decrease (20% of N_2O conversion) was in the case of the 1.4% Na* catalyst.

The best catalyst with 1.8 wt% K was chosen for further experiments. In Fig. 9 a comparison of N_2O conversions in the presence of O_2 and H_2O over 1.8% K and non-modified sample is shown. Strong inhibition was observed over the non-modified sample, while only a 25% decrease in N_2O conversion was determined over the 1.8% K sample. The negative effect of O_2 and H_2O is accumulative. This has been already observed in our earlier work dealing with the effect of oxygen and water vapor on catalytic activity of Co–Mg–Mn–Al mixed oxide catalyst for N_2O decomposition [38,43] and in other works dealing with N_2O decomposition over calcined hydrotalcites [22,36]. Competitive adsorption of H_2O on the N_2O decomposition active sites is expected. According to the literature, the alkaline metals cause an increase of catalytic activity for N_2O decomposition, namely in the wet stream [24]. In both cases, the inhibition was fully reversible and N_2O conversions were recovered when oxygen and water vapor were eliminated from the feed.

A comparison of catalytic performances in inert gas and in a typical waste gas composition downstream of the NO_x emissions reduction technology (0.1 mol% N_2O, 5 mol% O_2, 50 ppm NO, 0.9 mol% H_2O) over 1.8% K catalyst is shown in Fig. 10. In the case of N_2O catalytic decomposition in a typical real waste gas, the conversion curve was shifted towards higher temperature in comparison with the measurement in inert gas. $T_{50\%}$ (temperature at which N_2O

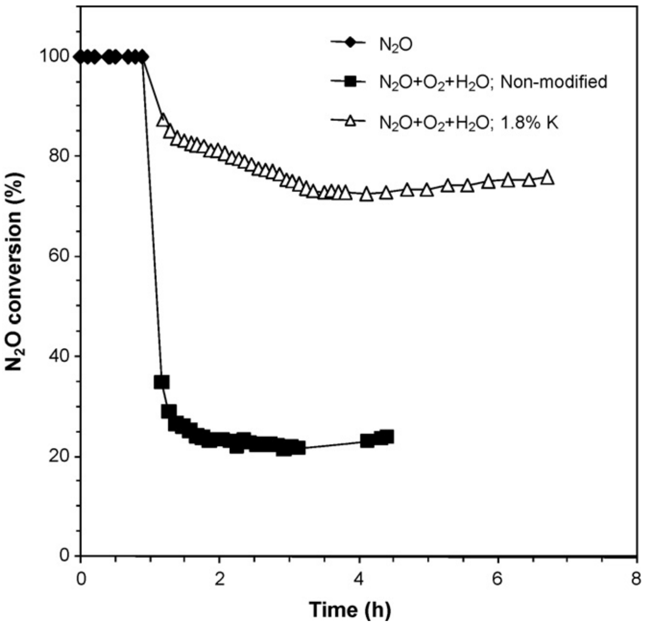

Fig. 9. Influence of O_2 and H_2O on the N_2O conversion over Co–Mn–Al mixed oxide and Co–Mn–Al mixed oxide modified by 1.8% K. Conditions: temperature 450 °C, 0.1 mol% N_2O in He, 5 mol% O_2, 4 mol% H_2O, SV = 20 l g^{-1} h^{-1}.

conversion is 50%) increased from 329 to 414 °C. It is worth noting that N_2O conversion of 90% was reached at 450 °C.

Taking into account the leaching effect which water may have on alkali cations, accelerated tests with high concentrations of all inhibition substances (H_2O, NO, NO_2 and O_2) were used to verify the stability of the catalytic performance for the 1.8% K and non-modified catalysts. N_2O conversions were controlled at reference conditions (0.1 mol% N_2O in helium). The results shown in Table S2 (see the Supplementary material) reveal the superior stability of both catalysts. N_2O conversions at reference conditions were the same as in the beginning of the measurements; therefore it is evident that the inhibition by H_2O, NO_x and O_2 was fully reversible.

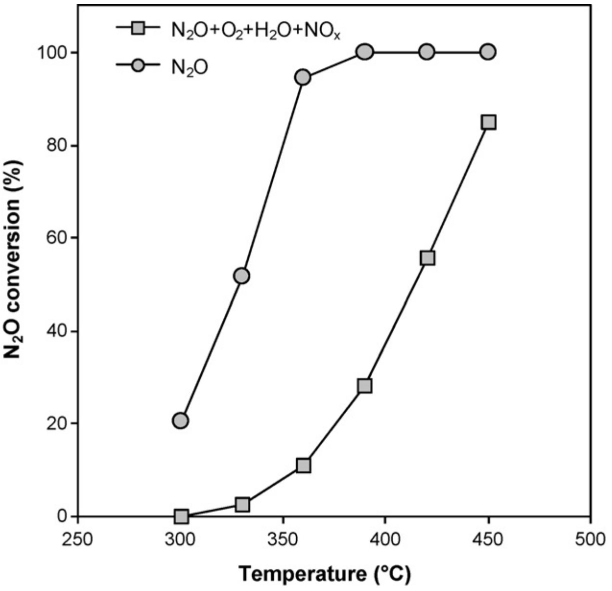

Fig. 10. Temperature dependence of N_2O conversion in inert and simulated process gas over Co–Mn–Al mixed oxide modified by 1.8% K. Conditions: 0.1 mol% N_2O, 5 mol% O_2, 0.005 mol% NO, 0.9 mol% H_2O in He, SV = 20 l g^{-1} h^{-1}.

4. Conclusions

Small amounts of alkali (Li, Na, K), rare earth (La, Ce) and noble metals (Pd, Pt) were examined as promoters in Co–Mn–Al mixed oxide with the aim to improve its activity for N_2O catalytic decomposition. The promoters were added to the parent Co–Mn–Al mixed oxide by applying two methods: (i) the promoter was added during the coprecipitation of the LDH precursor or (ii) the promoter was added by the impregnation of the parent Co–Mn–Al mixed oxide catalyst obtained after a thermal decomposition of the LDH precursor. The method applied for the modification of the catalyst with promoters affected the reducibility of the prepared catalysts; its effect on their activity in N_2O decomposition was less evident.

Only subtle changes in catalytic performance were observed after the modification of the Co–Mn–Al mixed oxide with Pd, Pt, La, or Ce. Opposite to this, substantial differences in N_2O conversion were observed over the catalysts modified with alkali metals. The catalytic activity of the Co–Mn–Al mixed oxide was remarkably enhanced due to the promotion of potassium. The addition of sodium also increased the N_2O conversion, while a decrease of N_2O conversion was observed over Li-containing catalysts. The differences in catalytic activity produced by modification of the Co–Mn–Al mixed oxide with alkali metals can be caused by modification of electronic properties of the catalyst surface leading to changes in the oxygen-transition metal bond strength and oxygen mobility.

The Co–Mn–Al mixed oxide with 1.8 wt% K exhibited a high catalytic activity even under simultaneous presence of O_2, H_2O, NO and NO_2. The laboratory stability test revealed that the beneficial effect was maintained for 360 h. Such excellent performance highlights its great potential as an industrially important catalyst for N_2O abatement.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.03.058.

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