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N_2O catalytic decomposition and temperature programmed desorption tests on alkali metals promoted Co–Mn–Al mixed oxide

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ABSTRACT

A series of Co–Mn–Al mixed oxides modified with alkali metals (Li, Na, and K) were prepared from Co–Mn–Al layered double hydroxide and tested for N_2O catalytic decomposition in inert gas and in the presence of oxygen. Chemical analysis, XRD, N_2 sorption, TPD-O_2 and TPD-N_2O were used to characterize the catalysts. During TPD-O_2, higher amount of O_2 was desorbed from more active catalysts. The extent of O_2 inhibition related to the degree of surface coverage by oxygen.

1. Introduction

Nitrous oxide, N_2O, is one of the most harmful gases in our environment because of its contribution to the depletion of the stratospheric ozone layer and high global warming potential. N_2O catalytic decomposition represents the solution for the reduction of N_2O emissions from chemical industry. The finding of catalyst with sufficient activity and stability in real off-gas conditions is still a problem and requires research effort in this field.

Many different catalysts have been studied for this process during the last two decades [1]. Among them, mixed oxides prepared from layered double hydroxide (LDH) precursors offered favorable results [2–6]. Our current research efforts are aimed at the development of catalytic system based on alkali-promoted Co-containing mixed oxides prepared from LDH precursors; the application of catalysts in the low-temperature ($\leq 450\,^\circ C$) decomposition of N_2O emitted from nitric acid plants is expected. At these temperatures, the other gases present in the real waste gas can inhibit the reaction rate of N_2O decomposition. For example, O_2 and H_2O inhibition was observed over Co_3O_4 spinel catalyst [7] as well as over Co/Mg–Mn/Al spinel catalysts prepared from LHD precursors [8]. Benefit of alkali promoters consists in maintaining a high N_2O conversion also in wet gas [4,9]. The concept of alkali metals doping in the deN_2O catalysis has been well established over spinel catalysts by Kotarba group [10–12] and is associated with beneficial influence of the electronic properties of the catalysts.

The decomposition of N_2O proceeds via oxidation–reduction mechanism [13]. It consists of three elemental steps expressed by Eqs. (1)–(3). Eq. (3) needs to be viewed as a more complex process, which proceeds differently on various catalysts. Our recent mechanistic kinetic study of N_2O decomposition over Co–Mn mixed oxide prepared from LDH precursors [14] indicated that recombination of adsorbed O species (Eq. (3)) proceeds in less extent and Eley–Rideal mechanism (Eq. (2)) is the main route of the O_2 desorption. The O_2 desorption was reported as the rate-determining step of the N_2O decomposition over cobalt-spinel catalysts [1].

$$N_2O + * \rightarrow N_2 + O* \quad (1)$$

$$O* + N_2O \rightarrow N_2 + O_2* \quad (2)$$

$$2O* \leftrightarrow O_2 + 2* \quad (3)$$

In this study, we used the temperature programmed desorption (TPD) technique for the investigation of the relationship between N_2O catalytic decomposition and O_2 desorption properties because oxygen plays an important role as inhibitor in the N_2O decomposition reaction. In order to examine the ability of the catalyst surface to bind oxygen, TPD of O_2 was carried out to contribute to the N_2O decomposition mechanism. TPD of O_2 was measured with catalysts

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

Sample	Promoter content (wt%)	Promoter molar content (mol/100 g)	SBET (m^2/g)	N_2O conversion[b] (%)
Non-modified	0	0	93	96
0.3% Li[a]	0.26	3.8×10^{-2}	100	87
1.4% Na[a]	1.39	6.0×10^{-2}	91	82
1.8% K	1.76	4.5×10^{-2}	98	100

[a] Catalyst prepared by impregnation method.

[b] Conditions: temperature 450 °C, 0.1 mol% N_2O + 5 mol% O_2 in He, SV = 20 l g^{-1} h^{-1}.

pre-treated by O_2 or N_2O and the N_2O decomposition was performed in O_2-free and O_2-rich atmosphere. The Co–Mn–Al mixed oxide with Co:Mn:Al molar ratio of 4:1:1 has been found as the most active catalyst for N_2O decomposition among all LDH-related catalyst tested by our group both in inert gas and in the presence O_2 or O_2 and H_2O [8,15]. For that reason this Co–Mn–Al mixed oxide modified with nearly the same molar content of alkali metals (Li, Na, and K) was chosen for present experiments.

2. Experimental

The Co–Mn–Al LDH precursor with Co:Mn:Al molar ratio of 4:1:1 was prepared by coprecipitation of corresponding nitrates and calcined at 500 °C in air. The obtained catalyst was labeled as "non-modified". Samples modified with promoters were prepared by two methods: (i) the "non-modified" mixed oxide was impregnated in solutions containing the promoter (aqueous solutions of $LiNO_3$ or $NaNO_3$) and (ii) the washed precipitate of Co–Mn–Al LDH precursor was dispersed in an aqueous solution of KNO_3 and the dried filtration cake was calcined at 500 °C in air. Details of the catalysts preparation can be found in [16].

Surface areas of the prepared catalysts were determined by N_2 adsorption/desorption at −196 °C using an ASAP 2010 instrument (Micromeritics, USA) and evaluated by the BET method.

The content of components in the catalysts was determined by atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES) after the dissolution of the samples in hydrochloric acid.

Powder X-ray diffraction patterns were recorded using a Seifert XRD 3000P instrument with Co Kα radiation (λ = 0.179 nm, graphite monochromator, goniometer with the Bragg–Brentano geometry) in 2θ range from 20 to 120°, step size 0.02°. For refinement of lattice parameters and estimation of the mean coherence length (approximately equal to crystallite size), DiffracPlus Topas, release 2000 (Bruker AXS, Germany) was used. The structural models were taken from the Inorganic Structure Database (ICSD), Retrieve 2.01 (FIZ Karlsruhe, Germany).

Temperature programmed desorption tests (TPD-O_2, TPD-N_2O) were carried out with a sample amount of 0.1 g. The catalysts were pretreated in He flow (50 ml/min) at 450 °C for 1 h and then cooled to 40 °C in the case of O_2 adsorption (TPD-O_2). A mixture of 5% O_2/He (30 ml/min) was introduced as the adsorbate gas at 40 °C for 1 h. Then the system was purged by He (30 ml/min) until no change in the O_2 signal was detected. The catalyst was heated with rate 20 °C/min to 450 °C. In case of N_2O adsorption (TPD-N_2O), the system was cooled to 400 °C after catalyst activation in He (450 °C, 1 h) and 1% N_2O/He mixture was used as the adsorbate gas (30 ml/min, 1 h). The catalyst was cooled down to 40 °C in the same flow for 10 h and then a He flow was substituted for the N_2O/He flow. After 1 h the system was purged and the catalyst was heated in He (30 ml/min) with rate 20 °C/min to 450 °C. In both cases the mass numbers m/z 32 – O_2, 44 – N_2O, and 30 – NO were monitored by an RGA 200 quadrupole mass spectrometer (Stanford Research Systems, Prevac) during the heating. The TPD results were evaluated using the OriginPro 8 software with an accuracy of ±5%.

N_2O catalytic decomposition was performed in an integral fixed bed stainless steel reactor of 5 mm internal diameter in the temperature range from 300 to 450 °C at atmospheric pressure. The catalyst bed contained 0.1 g of the sample with a particle size of 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 or 0.1 mol% N_2O and 5 mol% O_2 in helium. The reactor was heated by a temperature-controlled furnace. Before each run, the catalyst was pre-treated by heating it in a He flow 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. GC/TCD and RGA 200 quadrupole mass spectrometer (Stanford Research Systems, Prevac) was used for N_2O analysis (m/z = 44). Details of the GC analysis can be found in [9].

3. Results and discussion

The physicochemical properties of the prepared catalysts are summarized in Table 1. Surface areas of the promoted samples were similar compared to the non-modified sample. The Co–Mn–Al mixed oxide with spinel structure was found in the powder XRD pattern of the non-modified sample as it was reported formerly [17,18]. The presence of K and Na did not cause changes in the powder XRD patterns, while a slight decrease in the lattice parameter of the Li-containing catalyst was observed.

The temperature dependencies of N_2O conversions over Co–Mn–Al mixed oxide modified with Li, Na, and K are shown in Fig. 1. The catalyst containing K and Na showed higher catalytic activity in comparison with the non-modified one. On the contrary, the activity of the catalyst modified with Li was lower. A different activities order was observed when the N_2O decomposition proceeded in the presence of oxygen (Table 1). No oxygen influ-

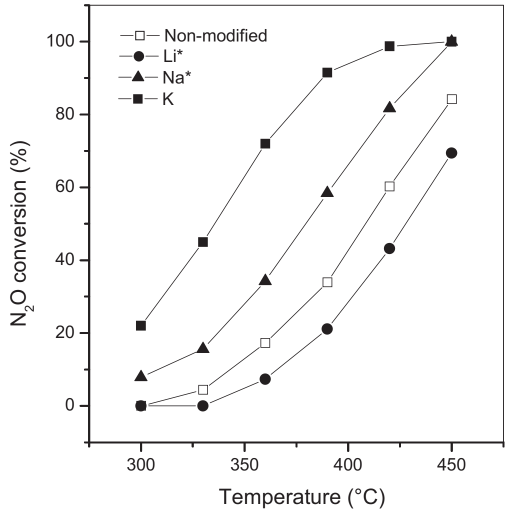

Fig. 1. Temperature dependence of N_2O conversion over Co–Mn–Al mixed oxide catalysts modified with alkali metals; (impregnated catalysts are labeled as *). Conditions: 0.1 mol% N_2O in He, SV = 60 l g^{-1} h^{-1}.

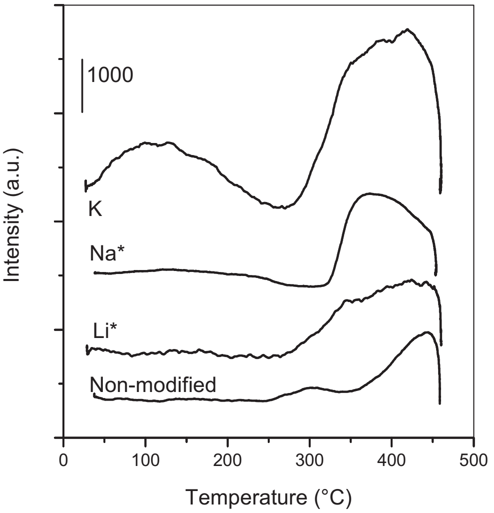

Fig. 2. TPD-O_2 patterns of the Co–Mn–Al mixed oxides modified with alkali metals.

ence was observed on the most active K-containing catalyst. In the other cases, the decrease of N_2O conversion was observed in the following order: non-modified > Li > Na. The inhibition by gaseous oxygen indicated that the active sites for N_2O decomposition and the oxygen adsorption/desorption sites are basically the same. The inhibition by O_2 present in the feeding gas can occur only when there are free active sites on the catalyst surface. If the inhibition by O_2 does not occur, there can be several reasons why: (i) the catalyst surface has been already covered by O_2 during the decomposition of N_2O in helium. This oxygen can come from the decomposing N_2O molecule or it can be the readsorbed O_2 from the gas phase. The latter is plausible especially in the case of high conversions, where the greatest amount of O_2 comes from N_2O decomposition. (ii) The oxygen is not being adsorbed on the catalyst surface at given conditions at all. To find out the reason for the O_2 inhibition, TPD experiments of oxygen were carried out. The results over catalysts pretreated by O_2 (TPD-O_2) and by N_2O (TPD-N_2O) are shown in Figs. 2 and 3, respectively. From the different shapes of TPD-O_2 and TPD-N_2O patterns, amounts of desorbed O_2 and temperatures of desorption maxima (Table 2) it can be concluded that the O_2 adsorption from gaseous O_2 is different than those from the dissociated N_2O molecule. Based on our recent results [16], the release of oxygen from the spinel lattice cannot be also excluded in either case.

Focusing on TPD-O_2, the O_2 was desorbed in two temperature regions only from the K-containing sample. The low temperature peak with maximum around 115 °C can be attributed to weakly bonded O species which were not present on the catalyst surface when N_2O decomposition started. The high temperature desorption peak above 250 °C was observed in all TPD-O_2 patterns; it consisted of several overlapping peaks belonging to suprafacial O species [19] and proved O_2 adsorption in the temperature region where N_2O decomposition proceeded. Therefore, the O_2 inhibition over the Na- and Li-containing and the non-modified catalysts was explained by the O_2 adsorption from gas phase according to Eq. (3), while high oxygen surface coverage during N_2O decomposition in helium can be assumed in the case of K-modified catalyst. It is noticeable that the highest amount of desorbed O_2 was found for the K-promoted catalyst, which was the most active both in inert gas and in the oxygen-containing atmosphere. Generally, beneficial influence of the K promoter on the electronic properties of the catalysts was mentioned as the reason of the increasing activity in N_2O decomposition [10].

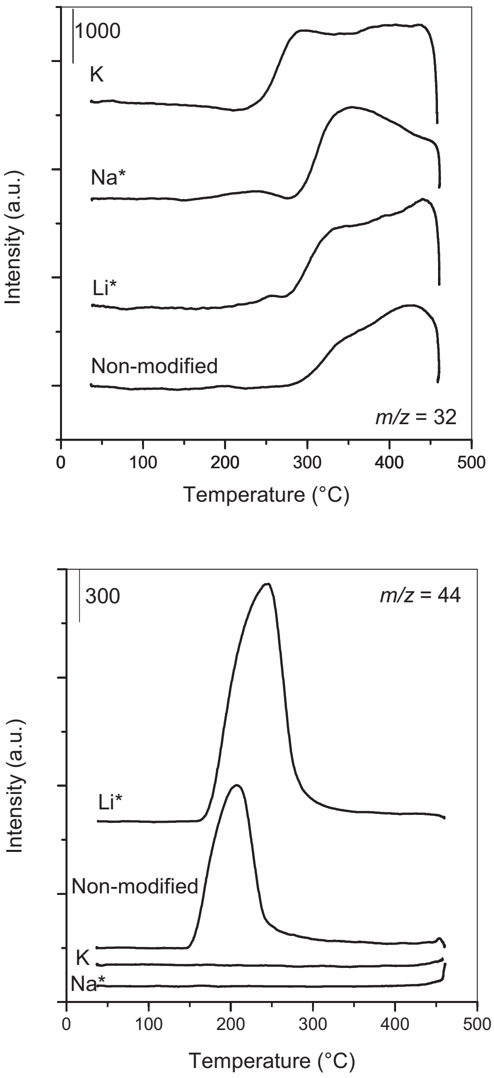

Fig. 3. TPD-N_2O patterns (signal 44 – N_2O, signal 32 – O_2) of the Co–Mn–Al mixed oxides modified with alkali metals.

When cooling down to room temperature, the decomposition of N_2O over the catalyst left adsorbed O species on the surface, which cannot be desorbed due to low temperature. These desorbed

Table 2
Evaluation of oxygen desorption during TPD-O_2 and TPD-N_2O over alkali promoted Co–Mn–Al mixed oxides.

Sample	Li[a]	Na[a]	K	Non-modified
TPD-O_2				
Peak maxima temperature (°C)	354, 422	377	117, 386, 420	301, 445
Desorbed O_2 (40–450 °C) (a.u.)	13.3	15.6	35.9	7.7
TPD-N_2O				
Peak maxima temperature (°C)	256, 341, 394, 440	237, 358, 450	258, 340, 450	200, 365, 427
Desorbed O_2 (40–450 °C) (a.u.)	31.6	26.8	32.0	21.4

[a] Catalyst prepared by impregnation method.

O species were detected during TPD-N_2O measurements (Fig. 3). Several overlapping peaks can be distinguished in the patterns at temperatures from 250 to 450 °C; they can be ascribed to the desorption of surface oxygen species ($-O$, $-O_2$), which are formed during the decomposition of N_2O [20–22]. The peaks above 350 °C could be attributed to the desorption of lattice and subsurface oxygen. We assume that the start of the O_2 desorption corresponds to the strength of oxygen bond with active site. Besides O species, small amount of adsorbed N_2O ($m/z = 44$) was also desorbed at temperature 150–300 °C from the Li-containing and non-modified catalysts (Fig. 3). It is supposed that this adsorbed N_2O did not participate in N_2O catalytic decomposition reaction [1,23]. In the proposed N_2O decomposition mechanisms, O_2 desorption is considered to be the slowest step and the oxygen bond strength is the decisive parameter for the catalyst activity. This agrees well with the fact that desorption of O species originated from N_2O started at temperatures similar to N_2O decomposition in the inert gas.

4. Conclusion

The N_2O catalytic decomposition over Co–Mn–Al mixed oxide modified with the same molar content of Li, Na, and K promoters was examined in an inert gas and in the presence of oxygen. TPD tests were carried out with catalysts pre-treated by O_2 or N_2O in order to discuss their catalytic performance in both environments. The effect of different alkali promoters on the rate of N_2O decomposition in an inert gas expressed as N_2O conversion was: K > Na > non-modified > Li while different order was obtained in an O_2-containing reaction mixture: K > non-modified > Li > Na.

For N_2O decomposition in O_2-free atmosphere, a higher amount of O_2 during TPD-O_2 pretreatment was desorbed from more active catalysts. No decrease of N_2O conversion after the addition of O_2 to the reaction mixture was observed over the most active K-promoted Co–Mn–Al mixed oxide, probably due to high surface oxygen coverage when the reaction proceeded in O_2-free gas.

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