Catalytic neutralization of nitrogen oxides on low-percentage Mn/ZnO catalysts, obtained via oxalate precursor

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Doped catalysts Mn/ZnO (Mn ≈ 0.035 wt.%) are obtained through decomposition of zinc oxalate. The precursors are prepared at two different $Zn^{2+}:C_2O_4^{2-}$ ratios in the initial solutions. In spite of the low manganese content, the $T_{\eta=50\%}$ decreased by 66ºC after the doping. It was established that in the case of doped samples the amount of reacted NO is higher than that of reacted CO. This fact, as well as the results from the TPD measurements, suggest that in the presence of Mn another type of catalytically active sites are being formed in addition to those existing on the surface of pure ZnO. As a result of this, along with catalyzed reduction of NO with CO, direct decomposition of NO to N_2 and O_2 is observed at temperatures higher than 300ºC.

INTRODUCTION

One of the important contemporary problems, which has not been optimally solved yet, is the neutralization of nitrogen oxides, especially in the presence of other oxidizing agents and most often in the presence of oxygen. In order to solve this problem, investigations are directed towards searching for new and more efficient catalysts. The neutralization of NO is mainly accomplished through a reduction process and therefore the search is focused on substances catalytically active in the reaction of NO reduction. In this respect, it seems that the most promising catalysts are those based on transition elements [1–11].

In the search for active catalyst, an essential problem is the choice of precursor. During the last years the application of the slightly soluble $ZnC_2O_4.2H_2O$ for preparing nanosized pure ZnO and ZnO doped with transition metal ions is increasing in importance [12–23]. An advantage of the oxalate precursor is its easy synthesis, the low temperature of decomposition, the liberation of a large amount of volatile substances (CO, CO_2, H_2O vapour) and the possibility of obtaining ZnO with different crystal forms and sizes. This explains the application of zinc oxalate as a precursor of catalysts [25–29]. Another advantage is the fact that the oxalates belonging to the magnesium series (Mg, Mn, Co, Fe, Ni and Zn) are isomorphous. This enables the modifying of the ZnO physical properties by doping of the precursor in the course of its synthesis [20–22, 28, 29].

In a previous publication [29], we have established that the doping of ZnO with low concentrations of Mn considerably promotes the catalytic activity of the oxide with respect to the oxidation of CO. For this reason, the aim of the present work was to investigate the catalytic activity of Mn/ZnO in the model reaction of NO reduction with CO by tracing the influence of the concentration of the oxalate ions during the precursor preparation.

EXPERIMENTAL

Synthesis of the samples

The samples of pure and manganese doped ZnC_2O_4 were synthesized by chemical reaction between $ZnSO_4$ and $K_2C_2O_4$ solutions at two different ratios of the initial molar concentrations of zinc and oxalate ions. Samples having a ratio $Zn^{2+}:C_2O_4^{2-}$ = 1:2 were prepared, denoted as the (1:2) series, while those with a ratio $Zn^{2+}:C_2O_4^{2-}$ = 1:1 were denoted as the (1:1) series. The experimental conditions were as follows: temperature T = 25.0 ± 0.5ºC; initial acidity of the system pH = 3.0 ± 0.1; synthesis duration 10 days

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under electromechanical stirring at 1000 r.p.m. For the preparation of the doped oxalate samples, a certain amount of the dopant (taken from 0.25 M $MnSO_4$ stock solution) was added to the $K_2C_2O_4$ solution before the mixing step. More details about the synthesis procedures and justification of the selected experimental conditions have been published previously [29].

In order to prepare pure and manganese doped ZnO, the synthesized oxalate precursors were calcined for 1 h in air at 470ºC. The oxalate decomposition was controlled by accounting for the changes in the weight of the sample.

The samples prepared in this way are denoted as ZnO (1:1), ZnO (1:2), 0.035 Mn/ZnO (1:1) and 0.039 Mn/ZnO (1:2). The labelling of the samples (1:2) or (1:1) indicates the initial ratio $Zn^{2+}:C_2O_4^{2-}$ during the precursor preparation, while the index 0.035 and 0.039 represents the content of manganese in the oxide sample in percentage by weight.

Sample characterization

The chemical composition of the samples was determined by means of atomic absorption analysis on a FAAS-SOLAAR M5 spectrometer. The X-ray diffraction (XRD) analysis was carried out on a Siemens powder diffractometer model D500. The scanning electron microscope (SEM) observation was carried out on a JEOL JSM–5510 apparatus. The electron paramagnetic resonance (EPR) spectra were registered using an ERS 220/Q instrument. The determination of the specific surface area of the samples was carried out by nitrogen adsorption at the boiling point temperature of liquid nitrogen 77.4 K using N_2/He mixture. The nitrogen adsorption isotherm was used to calculate the specific surface area (A_{BET}) according to the BET equation.

Catalytic activity testing

NO reduction reaction. The experimental runs to determine catalytic activity were carried out in a continuous flow reactor, described in details in [30]. The NO reduction with CO was investigated within the temperature range 20 – 400ºC. The catalytic activity tests were performed with a gas mixture: NO + CO + Ar, containing 1200 ppm NO and 1200 ppm CO. Argon (purity grade 99.99 vol.%) was used as a carrier at a gas hourly space velocity (GHSV) of 20º000 h^{-1}. A 1 cm^3 sample of

the catalyst (sieve fraction 0.3 – 0.6 mm) was charged in the reactor representing a quartz glass tube of inner diameter d = 10 mm.

Temperature-programmed desorption (TPD) was accomplished in the following way. A reaction mixture, consisting of CO and NO, was fed into the reactor in advance, passing through the catalyst bed at 25°C for 30 min. Thereafter, preserving the same temperature, argon was fed into the reactor and an increase in the temperature was started at a rate of 13ºC min^{-1} in the temperature interval 25–400°C. The inlet concentrations of NO and CO were continuously monitored by gas analysers. The outlet concentrations of NO and CO were controlled by "UNOR–5" (Maihak, Germany), while that of CO_2 was followed using "Infralyt 2106" (Germany). The N_2O concentration was measured spectrophotometrically by "Specord 75 IR" (Germany) with a 1 m folded path gas cell (Specac).

RESULTS AND DISCUSSION

Table 1 lists the content of Mn, the specific surface area of the catalyst samples, as well as the phase composition of the pure and Mn doped zinc oxide. The table also presents the degree of oxidation of the manganese ions, determined on the basis of the EPR spectra of doped samples. The EPR investigation revealed that the type of the spectrum does not depend on the $Zn^{2+}:C_2O_4^{2-}$ ratio in the initial solution [29]. The sextet signal typical of isolated Mn^{2+} ions was registered. This means that if Mn^{3+} and Mn^{4+} ions are present in the sample, their amount is negligibly small. The well-shaped well-separated peaks show that the doping agent is present only in small concentrations and is uniformly distributed inside the crystal lattice of ZnO.

The X-ray diffraction analysis of the oxide samples indicates the formation of wurtzite ZnO (JCPDS 36–1451) in all samples of both series [29], because of the low manganese content. However, the electron micrographs (Fig. 1) show some difference in the morphology of series (1:1) and (1:2). Polyhedral crystals are observed in the former case, while the prevailing number of crystals in the latter one has a prismatic form and they form aggregates. It is obvious that the gases,
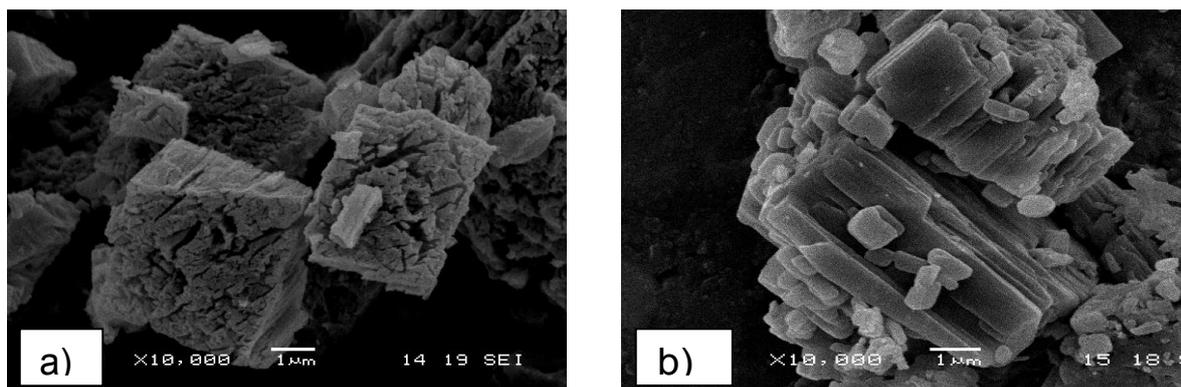
Fig. 1. Electron micrographs of a) ZnO (1:1); b) ZnO (1:2).

Table 1. Composition and properties of the samples studied

Sample	Content of Mn (wt. %)	Specific surface area A_{BET}, (m^2/g)	Phase composition (XRD)	Oxidation state of Mn (EPR)
ZnO (1:1)	-	27	ZnO	-
ZnO (1:2)	-	27	ZnO	-
0.035 Mn/ZnO (1:1)	0.0353	25	ZnO	Mn^{2+}
0.039 Mn/ZnO (1:2)	0.0385	25	ZnO	Mn^{2+}

which are liberated during oxalate decomposition, diffuse through the crystals in different ways, thus forming different types of channels. In the case of (1:1) series (Fig. 1a), pores and cracks on the surface of the polyhedra are observed, while in the case of (1:2) series the surface is smooth and the channels are probably located between the separate prismatic crystals. The doped ZnO possesses the same morphology.

Figure 2 represents the temperature dependence of the NO conversion degree for pure and manganese doped oxide samples. At the beginning of the studied temperature range, the reduction proceeds with low catalytic activity for all samples. However, the conversion with the non-doped samples begins at temperatures above 100ºC, while the doped samples already manifest activity at this temperature. Despite the low manganese content, the doping leads to a decrease of the starting temperature of NO active reduction with CO by 50ºC. At one and the same content of the active component, the sample belonging to the (1:2) series is more active than that of the (1:1) series. A possible cause is the more uniform distribution of manganese ions, which is associated with the different mechanism of inclusion that depends on the initial oxalate concentration [31]. A conversion degree of 70% for NO was achieved at 300ºC with the 0.039 Mn/ZnO (1:2) sample, while the same conversion degree was reached with the sample

0.035 Mn/ZnO (1:1) at 400°C. The studies revealed that with both samples under consideration, NO reduction with CO occurred with N_2 formation. Within the entire investigated temperature interval no N_2O was registered.
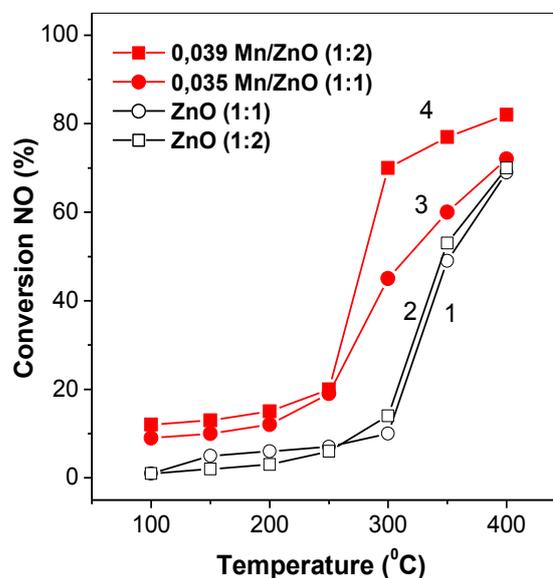
Fig. 2. Temperature dependence of the NO conversion degree in the reaction NO+CO: curve 1 - ZnO (1:1), curve 2 - ZnO (1:2), curve 3 – 0.035Mn/ZnO (1:1), curve 4 – 0.039Mn/ZnO (1:2).

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g. 3. Amount of NO (mmol.10^4/g.h) – curve 1, and amount of CO (mmol.10^4/g.h) – curve 2, reacted for sample 0.035 Mn/ZnO (1:1).

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Fig. 4. Amount of NO (mmol.10^4/g.h) – curve 1, and amount of CO (mmol.10^4/g.h) – curve 2 reacted for sample 0.039 Mn/ZnO (1:2).

Figures 3 to 5 juxtapose the temperature dependences of the reacted amounts of NO and CO by 1 g catalyst per 1 hour for each studied sample. Figure 3 refers to the 0.035 Mn/ZnO (1:1) sample, Figure 4 – to the 0.039 Mn/ZnO (1:2) sample, while Figure 5 – to the pure ZnO samples of both series. With the non-doped catalyst samples the quantity of reacted NO is equal to the quantity of reacted CO, while in the case of the doped samples there is some difference between the two quantities. In both cases, at temperatures higher than 300°C the amount of reacted NO is higher than that, stoichiometrically necessary for the reaction with CO. For the 0.039 Mn/ZnO (1:2) sample this difference is slightly bigger. These data show that in addition to the catalytic reduction with CO one should also suppose the occurrence of the reaction of direct NO decomposition. Such parallel reaction

Fig. 5. Amount of NO (mmol.10^4/g.h) reacted for samples ZnO (1:1) – curve 1 and ZnO (1:2) – curve 3, amount of CO (mmol.10^4/g.h) reacted for samples ZnO (1:1) – curve 2 and ZnO (1:2) – curve 4.
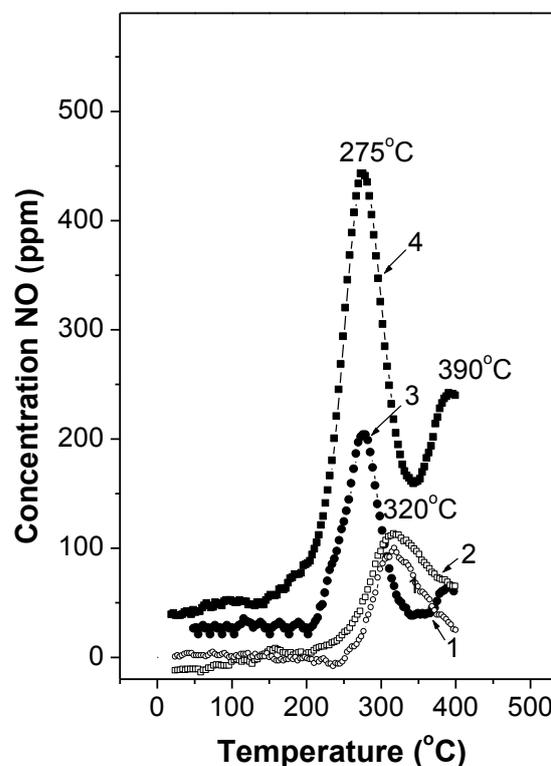
Fig. 6. TPD patterns of NO for the studied samples: ZnO (1:1) – curve 1 and ZnO (1:2) – curve 2, 0.035Mn/ZnO (1:1) – curve 3 and 0.039Mn/ZnO (1:2) – curve 4.

of direct decomposition of NO to N_2 and O_2 has also been observed for catalytic systems containing Ag and Pd [7, 32]. Therefore, two reactions are taking place on the surface of the doped catalyst – catalytic reduction of NO with CO and direct decomposition of NO.

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The above conclusion is confirmed by the results of the TPD measurements. Figure 6 presents the TPD patterns of NO for all studied samples after carrying out the catalyzed reduction of NO with CO. The patterns were recorded in a flow of Ar within the temperature interval $25 - 400$ºC. No peaks of CO and CO_2 desorption are observed within the entire studied temperature interval for all samples, which is an indication that CO is not adsorbed in any form on their surface. As far as the pure ZnO samples are concerned, a single desorption peak at 320°C is observed. In the case of the doped samples 0.035 Mn/ZnO (1:1) and 0.039 Mn/ZnO (1:2) two expressed NO desorption peaks are present in the pattern having maxima at 275ºC and ~390ºC. The NO is adsorbed on the surface of these samples in two different forms – one of which is weakly bound and the other has stronger bonding. These results imply that two different types of catalytically active sites are probably formed on the surface of doped samples.

The correlation between the quantities of reacted NO and CO in the case of non-doped samples, as well as the lack of CO desorption peaks, allow us to draw the conclusion that the probable mechanism via which the catalyzed reduction of NO with CO occurs on pure ZnO samples at temperatures higher than 250ºC belongs to the Eley-Rideal type. It occurs in accordance with Scheme (1): NO is adsorbed on the surface and thereafter CO from the gas phase reacts with it.

$$2\,NO + [CAC]_a \rightarrow NO[CAC]_a.NO$$
$$NO[CAC]_a.NO + 2(CO)_{gas} \rightarrow N_2 + 2\,CO_2 + [CAC]_a$$
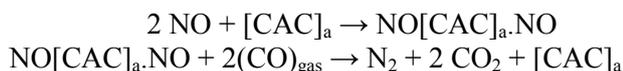
Scheme 1

Here [CAC] is the catalytically active complex on the surface of the sample, which, in our opinion, may comprise several active sites.

The difference in the reacted amounts of NO and CO in the case of the doped samples, as well as the second peak in the TPD-NO curves show that in parallel to the reactions described in Scheme (1), one should also suppose a direct decomposition of NO to $N_2 + O_2$ according to Scheme (2), which proceeds on a different type of catalytically active sites $[CAC]_b$ at temperatures ≥ 300ºC.

$$2\,NO + [CAC]_b \rightarrow NO[CAC]_bNO$$
$$\rightarrow N_2 + O_2 + [CAC]_b$$
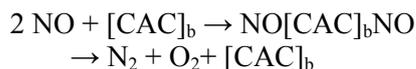
Scheme 2

Therefore, it may be assumed that two types of catalytically active complexes [CAC] are formed

on the surface of the samples in the presence of manganese. This is confirmed by the fact that there is only one peak of NO desorption in the TPD pattern of the spent ZnO catalyst, while in the case of doped samples two desorption peaks are observed. As was mentioned above, proceeding of such parallel reactions was observed with Ag- and Pd-doped catalysts [7, 32].

CONCLUSIONS

The studies carried out revealed that the co-crystallization method applied for doping ZnO with manganese leads to uniform distribution of the manganese ions inside the structure of ZnO and there is no interaction between them.

In spite of the low manganese content in the samples (0.035% and 0.039%), the catalytic activity tests demonstrated the effectiveness of doping in view of purifying gaseous fluids by NO_x removal – lowering of the temperature of active reduction by 50ºC, as well as increasing the conversion degree from 10% up to 70% at 300ºC. On the basis of TPD measurements it may be concluded that this is due to the weaker bonding of NO molecules on the surface of doped samples which facilitates their reduction. At one and the same dopant content, the sample of the 1:2 series was more active than the respective sample of the 1:1 series, probably due to the more uniform distribution of manganese ions on the former samples. A conversion degree of 70% was achieved at 300ºC with the 0.039Mn/ZnO (1:2) catalyst sample, while with the sample 0.035 Mn/ZnO (1:1) the same conversion was reached at 400ºC.

The obtained data also enabled drawing the conclusion that Mn doping leads to the formation of another type of catalytically active complexes $[CAC]_b$ in addition to those existing on the surface of pure ZnO ($[CAC]_a$). As a result of this, beside the NO reduction reaction with CO on $[CAC]_a$, above a certain temperature there occurs also direct decomposition of NO on $[CAC]_b$.

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КАТАЛИТИЧНА РЕДУКЦИЯ НА АЗОТНИ ОКСИДИ ВЪРХУ НИСКО-ПРОЦЕНТНИ Mn/ZnO КАТАЛИЗАТОРИ, ПОЛУЧЕНИ ОТ ОКСАЛАТЕН ПРЕКУРСОР

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(Резюме)

Катализатори Mn/ZnO (Mn ≈0.035 wt.%) са синтезиране чрез разлагане на дотиран цинков оксалат, получен при две различни съотношения Zn^{2+}:$C_2O_4^{2-}$ в изходните разтвори. Дотирането на ZnO води до понижаване на $T_{\eta=50\%}$ с 66°C, независимо от ниското съдържание на манган в пробите. Установено е, че при дотираните образци количеството реагирал NO е по-високо от това на реагирали CO. Този факт, както и данните от TPD измерванията, водят до предположението, че в присъствие на Mn на повърхността на катализатора се формират и друг тип каталитично активни центрове в допълнение на наличните при недотиран ZnO. В резултат на това, освен катализирана редукция на NO с CO протича и директно разлагане на NO до N_2 и O_2 при температури по-високи от 300ºC.