Catalytic activity of $(CaO)_{1-x}(ZnO)_x$ solids for the N_2O decomposition: relation with photoluminescence

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$(CaO)_{1-x}(ZnO)_x$ mixed oxides ($x = 0$–1), heated at 1423 K under atmospheric conditions, were checked for their catalytic activity in the N_2O decomposition in the temperature range of 450–650°C. Although the catalytic activity was measured in the dark, it was found to be linearly related with the photoluminescence intensity of the catalysts.

Keywords: $(CaO)_{1-x}(ZnO)_x$; catalytic activity; photoluminescence; N_2O decomposition

1. Introduction

Photocatalytic processes are favourable for environmental purification processes either in gas or liquid phase since they represent "clean" and inexpensive technologies [1]. The interest of researchers in the field of environmental catalysis using photocatalysts is focused either on studies related to water purification from organic contaminants [2,3] or on decontamination of gas streams [4]. It should also be mentioned that in the past, various researchers in the field of industrial catalysis have scrutinized various solids for their photoactivity [5,6]. Thus the established photocatalysts are mainly solids based either on TiO_2 or ZnO [7,8], while various doping procedures are often exploited in order to enhance the photocatalytic activity of such materials. On the other hand, reduction of NO_x emission from automobile and stationary sources has become one of the most important problems to be solved for environmental protection [9].

Recently, we have obtained, at room temperature, an intense photoluminescence from the $(CaO)_{1-x}(ZnO)_x$ solids in air [10], which is maximized in the case of 1% Zn addition to CaO ($x = 0.01$). In the present work, the photoluminescence behavior of $(CaO)_{1-x}(ZnO)_x$ mixed oxides is examined in relation to their catalytic activity for a de-NO_x process, namely the decomposition of N_2O. This pollutant has recently attracted the increased interest of many researchers working in the field of Catalysis and the Environment, since it is a green-house gas and it might also contribute to the destruction of the ozone layer in the stratosphere [11,12]. Although N_2O is not a pollutant in the strict sense, as are NO or NO_2, because it does not react in the atmosphere producing a photochemical smog, and is not dangerous to human itself, it has a minor contribution to the global warming. The reason for using its decomposition as a probe reaction for the activity of our solids, apart from the above reasons, stems from the fact that it is a reaction examined routinely by many workers and there is a wealth of information for catalytic activity on single oxide systems.

2. Experimental

Samples, of the general formula $Ca_{1-x}Zn_xO$ ($x = 0.000$, 0.005, 0.010, 0.050, 0.100, 0.300, 0.500, 0.700, 0.900, 0.950, 0.990, 0.995 and 1.000) were prepared by mixing calculated amounts of CaO (Fluka, p.a.) and ZnO (Merck, p.a.) powder oxides, grinding and heating repeatedly under atmospheric conditions at 1423 K. Then, the solids were left to cool down slowly at room temperature in order to obtain the hydroxylated oxide precursors. As the thermogravimetric experiments showed, the latter are converted completely to oxides after heating at 650°C in He flow for 1/2 h. Another pretreatment was used to obtain the $(CaO)_{1-x}(ZnO)_x$ oxides for XRD, as well as for photoluminescence measurements [10]. The oxides are designated as CZ:*y*, where *y* is defined as the percentage of Zn atoms over the total amount of metal (Zn + Ca) atoms in the solid [$y = 100\mathrm{Zn}/(\mathrm{Ca} + \mathrm{Zn})$].

The catalytic activity of the solids was checked in the dark, in a lab-scale plug-flow reactor (PFR) similar to that described in refs. [13,14]. Helium plus N_2O at a ratio of 2 : 1 and a total flow of 75 $cm^3\ min^{-1}$ were allowed to flow through the reactor, consisting of a silica tube 1 cm in diameter with a perforated glass bed, on which 0.2 g of the solid was placed. The system was heated by a tubular furnace to within ±2°C. Analyses of the reactants and the products were carried out by sampling 1 cm^3 of the gases to a Varian 3700 gas chromatograph equipped with a TCD, with He as carrier gas, and connected to a Milton Roy PC-8023BE-N integrator system. The column used for analysis was 1 m × 3.17 mm (1/8 in) stain-

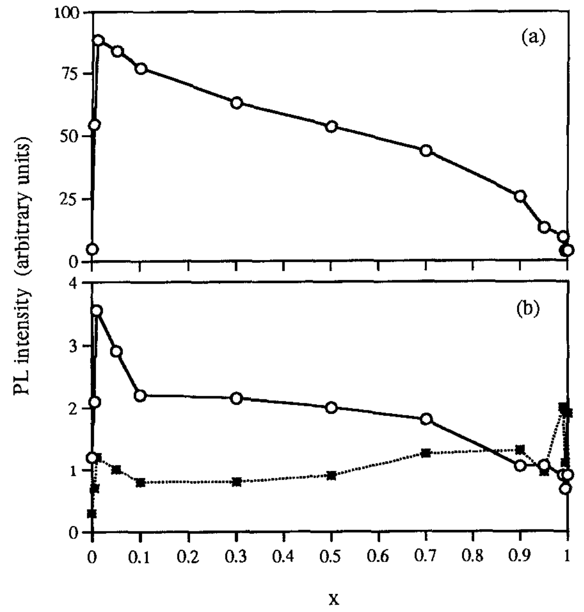

Fig. 1. Photoluminescence intensity versus Zn content, x, of the $(CaO)_{1-x}(ZnO)_x$ solids: (a) The main, blue emission ($\lambda = 435$–448 nm), recorded by excitation at 215 nm. (b) (○) The blue-violet emission ($\lambda = 406$–440 nm) and (■) the green emission ($\lambda = 508$–527 nm), recorded by excitation at 240 nm.

less steel containing 5A molecular sieves. The experiments took place in 50°C intervals in the region of 450–650°C. The catalytic activity of the oxides was measured in situ in the catalytic reactor, after 1/2 h calcination of their precursors at 650°C in He flow. In each experiment the reaction rate was calculated as the amount reacted per unit mass of the catalyst. The XRD patterns as well as the photoluminescence spectra of the oxides are given elsewhere [10].

3. Results and discussion

We have recently recorded an intense luminescence from the $(CaO)_{1-x}(ZnO)_x$ oxides, by means of high UV energy excitation (5–6 eV). The emission, as well as the excitation spectra recorded, are given analytically in ref. [10]. A broad emission band, peaking at the blue ($\lambda = 435$–448 nm) was obtained from the CZ:0–70 solids by excitation at 215 nm, e.g. near their maximum excitation wavelength (200–218 nm). However, a significant contribution of a green emission component ($\lambda = 508$–527 nm) is clear in the case of the other solids, as the spectra, especially those recorded with 240 nm excitation, show [10]. The intensity of the main emission band vary across the CZ:y solids as shown in fig. 1a. The 0.5–70% Zn addition to CaO results in a dramatic enhancement of the photoluminescence intensity, which is maximized at 1% addition. In fig. 1b the photoluminescence intensity of both, the blue-violet ($\lambda = 406$–440 nm) and the green ($\lambda = 508$–527 nm) emission components, recorded with 240 nm excitation, are given. Although the blue-violet emission component dominates over the CZ:0–70 solids spectra, in this case, the green emission component clearly dominates over those of CZ:90–100 solids.

The observed catalytic activities of CZ:y solids are presented in table 1 in the form R (mol/(g s)) for various temperatures. It must be stressed here that all the CZ:y oxides were found to be rather inactive after high-temperature calcination, followed by a quick removing from the furnace at about 400°C. This is probably a result of the "sintering" the samples undergo due to the high-temperature treatment. However, the oxides obtained by thermal treatment of their hydroxylated precursors at mild conditions, e.g. calcination at 650°C in He flow, possess a remarkable catalytic activity. Thus, the CZ:0–70 solids are active for the N_2O decomposition, while the CZ:90–100 are rather inactive. Therefore, both active centers and a favourable texture should appear under these conditions, at least in the case rich in Ca oxides.

The CZ:y solids showed, by XRD examination, the crystal phases of the parent oxides in varying ratios [10]. However, neither photoluminescence nor catalytic

Table 1
Reaction rate (mol g^{-1} s^{-1}) for the N_2O decomposition over $(CaO)_{1-x}(ZnO)_x$ catalysts at different temperatures

Sample	$R \times 10^5$ (mol $g^{-1}s^{-1}$)				
	450°C	500°C	550°C	600°C	650°C
CZ: 0.00	0.279	1.023	2.742	5.506	–
0.5	1.088	3.645	6.919	8.705	–
1	0.781	2.883	6.175	8.454	–
5	0.930	3.097	6,268	8.314	–
10	1.004	3.422	6.854	8.370	–
30	0.372	1.488	4.018	7.710	–
50	0.363	1.776	4.334	6.798	–
70	0.288	1.534	3.878	6.640	–
90	–	–	–	–	0.297
95	–	–	–	–	0.074
99	–	–	–	–	0.139
99.5	–	–	–	–	0.028
100	–	–	–	–	–

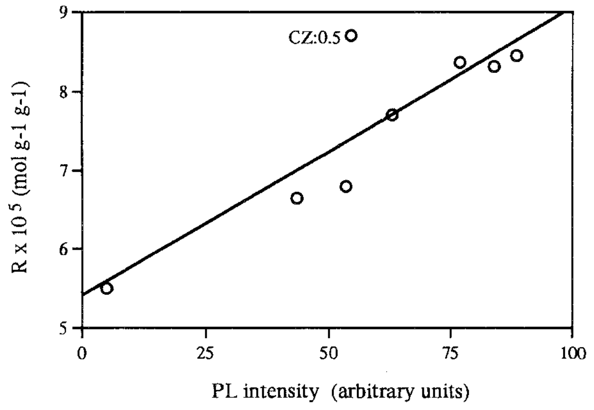

Fig. 2. Relation between the catalytic activity for the N_2O decomposition at 873 K and the recorded photoluminescence at 435–448 nm ($\lambda_{ex} = 215$ nm).

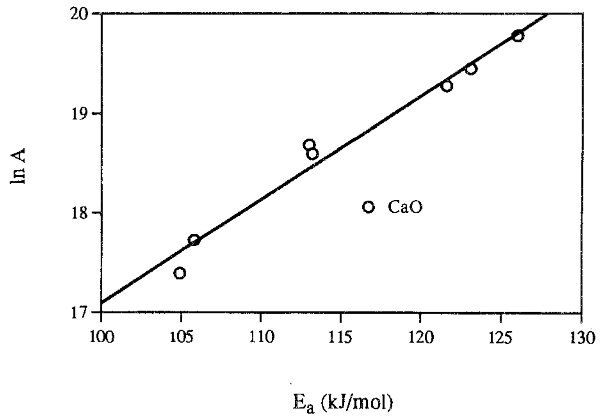

Fig. 3. Compensation effect for the N_2O decomposition over $(CaO)_{1-x}(ZnO)_x$ catalysts.

behavior of the samples are affected in an expected way by the dominating XRD phase. A synergistic action between CaO and ZnO is clear in both catalytic and photoluminescence behavior of CZ:y solids.

As noticed above, the catalytic activities of the mixed oxides were determined under dark conditions. Nevertheless, the catalytic activity is really correlated to the luminescence from the oxides: The oxides with blue dominant photoluminescence (CZ:0–70) are active, while those with increased green luminescence (CZ:90–100) are inactive for the tested reaction (fig. 1, table 1). To be more precise, the appearance of considerable activity coexists with the prevalence of blue emission. Besides, the photoluminescence intensity of the oxides $(CaO)_{1-x}(ZnO)_x$ is linearly related with their activity for the N_2O decomposition (fig. 2). We notice that, although the emission spectra were not corrected for the photomultiplier response, the pictures obtained in figs. 1 and 2 are not affected, as quoted for emission intensities of a very similar wavelength.

The activation energies for the N_2O decomposition were determined by using first-order kinetics according to the methodology discussed elsewhere [13,14]. The calculated apparent activation energies E_a as well as the pre-exponential factors ln A are shown in table 2.

The values of E_a do not correlate in any meaningful way to the photoluminescence activity. Nevertheless E_a and ln A show the well known compensation effect (fig. 3).

The linear relationship observed between catalytic activity and photoluminescence suggests some similarity in the mechanisms of the two processes. The photoluminescence from the CZ:y solids is possibly a result of recombination processes between electrons and holes, involving oxygen anion vacancies, as well as photogenerated F^+ and F centres, according to the scheme given in ref. [10]. Then, blue emission could be the result of one F^+ electron recombination with a hole into the O^- hole level, while green emission could be the result of one-electron trapping by a present F^+ centre [10]. The dominating emission from the CZ:0–70 solids is blue, because the recombination processes proceed mainly through the F^+ centres [10]. Therefore, the correlation of fig. 2 indicates that electron transfer processes during catalytic reaction may also involve oxygen anion vacancies as well as formed F^+ centres.

In fact, the blue emission intensity may represent a measure of the concentration of the F^+ type defects that are formed during the illumination [10]. Thus, the correlation of fig. 2 suggests that the N_2O decomposition proceeds over the CZ:0–70 catalysts through oxygen anion vacancies, especially through F^+ centres. These defects could be easily formed during the catalytic process over the CZ:y solids, via the trapping of one electron by an oxygen anion vacancy, present as a result of their treatment.

We consider that Zn^{2+} cations, although they dispose closed d shells, facilitate the catalytic, as well as the photo-processes over the CZ:0.5–70 solids, because they can easily trap electrons thereby converting into the unstable Zn^+ cations which, in turn, can easily give back electrons to the oxygen vacancies. Thus, the electron

Table 2
Calculated apparent activation energies E_a and pre-exponential factors ln A for different values of x

	x in $(CaO)_{1-x}(ZnO)_x$							
	0.000	0.005	0.010	0.050	0.100	0.300	0.500	0.700
E_a (kJ/mol)	116.7	105.8	113.2	104.9	113.0	123.1	121.6	126.0
ln A	18.06	17.72	18.60	17.39	18.69	19.45	19.28	19.78

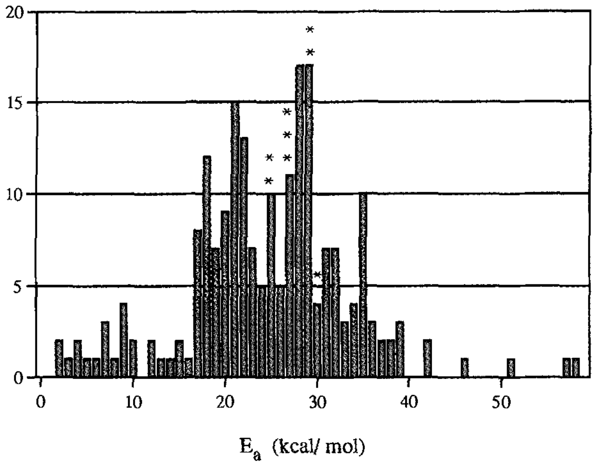

Fig. 4. Histogram of apparent activation energies for N_2O decomposition on various solids as collected and summarized by Larsson (dark bars) [22]. The stars represent the values from the present work.

transfer processes, required for the catalytic reaction to proceed, are facilitated by the intermediate formation of F^+ type defects, through the oxygen anion vacancies. A dynamic equilibrium between Zn^+ and Zn^{2+} cations, which may be established during the catalytic process, ensures the unhindered creation and annihilation of F^+ centres. Therefore, F^+ centres neighbouring to Zn^+ cations seem to be the active centres for the N_2O decomposition over the CZ:0.5–70 oxides. Isolated Zn^+ cations, which can also act as active centres, are possibly the cause of the CZ:0.5 sample inclination in fig. 2.

The role of F^+ centres in chemisorption over irradiated CaO is known [15,16]. Besides, surface F^+ centres have been assumed in the past to be the active donor centres for the N_2O decomposition over simple oxides [17–19]. However, low coordinated surface ions are believed to be the active centres in heterogeneous catalysis [20] as well as in photocatalysis [21] over high surface area alkaline earth oxides. Our results do not agree with an assignment of photoluminescence and catalysis over CZ:*y* solids to such ions, which are the result of a high temperature treatment of the oxides in vacuo, a procedure quite different than this followed here.

At this point a comparison of catalytic activity of our solids with other data from literature concerning the same reaction is in order. In fig. 4 the apparent activation energies calculated in the present work are compared with 212 other values of E_a collected and summarized by Larsson [22].

The comparison of the reaction rates with literature data is less straight since various authors employed different expressions about it. Nevertheless a comparison with perovskites containing transition metal elements is shown in table 3, the data taken from refs. [23,24].

It can be seen that our solids are on the average one order of magnitude less active as compared to those perovskites. Keep in mind, that perovskitic solids are often as active as noble metals for redox reactions [25]; but such a difference is perhaps justified since neither zinc nor calcium contain d-elements which are usually considered as prerequisites for this reaction. Besides, our experiments were carried out in the dark, and under these conditions the activity is not expected enhanced by the photoeffects discussed.

In conclusion, although the data of photoluminescence and catalytic activity were recorded separately,

Table 3
Comparison of the catalytic activity of some perovskite catalysts cited in literature, with the present work

Catalyst	Temperature (°C)	Rate constant	Units	Ref.
$LaMnO_3$	360	3.553×10^{-5}	$mm^{1/2}\ s^{-1}\ m^{-2}$	[23]
$NdMnO_3$	410	1.055×10^{-5}	"	[23]
$SmMnO_3$	440	2.208×10^{-6}	"	[23]
$GdMnO_3$	410	2.552×10^{-5}	"	[23]
La_2CuO_4	450	2.90×10^{-4}	s^{-1}	[24]
	480	5.33×10^{-4}	"	[24]
Pr_2CuO_4	440	7.76×10^{-4}	$mm^{1/2}\ s^{-1}$	[24]
	490	14.50×10^{-4}	"	[24]
Nd_2CuO_4	440	17.60×10^{-4}	"	[24]
	480	27.80×10^{-4}	"	[24]
Sm_2CuO_4	460	12.50×10^{-4}	"	[24]
	480	17.80×10^{-4}	"	[24]
Gd_2CuO_4	460	9.00×10^{-4}	"	[24]
	480	13.70×10^{-4}	"	[24]
CZ:0.5	450	3.267×10^{-5}	$mol\ g^{-1}\ s^{-1}\ atm^{-1}$	this work
	500	1.094×10^{-5}	"	this work
CZ:1	450	2.345×10^{-5}	"	this work
	500	8.657×10^{-5}	"	this work
CZ:5	450	2.793×10^{-5}	"	this work
	500	9.300×10^{-5}	"	this work
CZ:10	450	3.015×10^{-5}	"	this work
	500	1.028×10^{-5}	"	this work

the relation between the two is beyond doubt. Besides, the enhanced photoluminescence of the CaO solids doped with 1% Zn make them very promising photocatalysts for de-NO_x or other photosensitive processes.

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