

Doped with Cu and Mn zinc oxide catalysts for oxidation of CO in noxious gas emissions

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Received January 30, 2017; Revised February 16, 2017

Dedicated to Acad. Bogdan Kurtev on the occasion of his 100th birth anniversary

In the present work doped with Cu and Mn zinc oxide is investigated as catalyst for oxidation of CO. The doped zinc oxide samples are synthesized from carbonate, acetate and nitrate precursors and from activated doped ZnO. The content of Mn and Cu in the catalyst compositions is less than 1 wt %. For structural, textural and morphological characterization of the samples trivial methods were used: Atomic Absorption Spectroscopy (AAS), X-ray Diffraction (XRD), BET surface area analysis, X-ray Photoelectron Spectroscopy (XPS). Measurements of the catalytic activity were performed. A correlation between the type of precursor used for ZnO synthesis and the catalytic conversion has been established. The conversion reaches the highest values of 50% at 290 °C and 95% at 320 °C for Cu doped sample when activated ZnO is used as a carrier. ZnO synthesized by trivial method from carbonate precursor has 50% conversion at about 35 °C higher temperature than the activated sample. The results of recent investigation show high perspective of the catalysts, synthesized from activated carbonate precursors.

Key words: zinc oxide; manganese; copper; doping; carbon monoxide oxidation

INTRODUCTION

The accelerated development of energy and chemical industries leads to serious contamination of the environment. The existence of noxious emissions in the air such as CO, NO_x, H₂S and hydrocarbons from the internal combustion engines and the industry is a serious ecological problem. The catalytic disposal is one of the effective way for downgrading these contaminations [1–5]. Carbon monoxide can be removed by complete catalytic oxidation, achieved by catalysts with high efficiency and stable at dynamic variable conditions [6–8]. Precious metals based catalysts have widespread application in purification of waste gases [6–12]. These catalysts used in industrial practice have a number of disadvantages. They are expensive, due to the use of active components with high price, as well as the use of complex technological methods for production of the active phases. The searching of catalytic compounds with optimal composition and parameters is still actual question [1]. Another widespread catalytic group is that with high content of oxides and compounds of 3d transition metals [2, 10]. There is enhanced interest to the recently synthesized catalysts

consisting low per cent content of active phases Cu and Mn [8, 10, 13]. The choice of the precursor for the synthesis of active catalyst is essential. In some cases the change of the synthesis route can change the structure of materials, which is useful for practical application [8]. In the field of catalysis basic properties such as activity and selectivity are seriously influenced by the nanostructure of materials, which highly depends on the synthesis conditions [7, 9–12]. During the last years there is increasing interest to ZnO, obtained from different precursors. This is due to the specific chemical, surface and microstructure properties of this oxide, depending on the synthesis conditions and various methods of preparation. Participation of dopants in ZnO based catalysts leads to changes in the structure and texture characteristics, higher catalytic activity and stability and better performance in practice [6, 14–17]. That is why doped and activated ZnO is promising material because of its relatively low price and wide scale application as catalyst [12, 13, 18].

The aim of the present work is synthesis of ZnO based phases from different precursors (nitrate, acetate, carbonate) doped with Cu and Mn (<1 wt.%) and investigation of their catalytic activity. The content of Cu and Mn is lower than 1 wt.% and

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the obtained samples are from nitrate, acetate and carbonate precursor solutions.

EXPERIMENTAL

Several samples were obtained and named as follows:

A) From nitrate precursor: *MnZnO nitrate and CuZnO nitrate*

From acetate precursor: *MnZnO acetate and CuZnO acetate*

From carbonate precursor: *MnZnO carbonate and CuZnO carbonate*

Doped with Mn and Cu samples of ZnO were obtained from zinc nitrate, acetate and carbonate precursors.

$Zn(NO_3)_2 \cdot 4H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$ solutions were thermally decomposed for the preparation of ZnO. Small amounts of solutions of respective dopants - $Mn(NO_3)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ were also added in defined ratio. For preparation of ZnO from carbonate, solutions of 0.8M Na_2CO_3 , 0.4M $ZnSO_4 \cdot 7H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ were used in defined ratio. For preparation of the catalysts, the corresponding precursors were heated for 3 h at 400 °C in air.

B) From carbonate precursor by deposition: *CuZnO deposition*

Previously obtained carbonate precursor was treated by aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ to lay the active phase by deposition method.

C) Previously activated Zinc oxide: *MnZnO activated, CuZnO activated*

Precursor of activated ZnO was prepared using method described in Bulgarian patent № 28915/1979. The active, Cu and Mn (~ 0.2 wt.%) phases of the supported catalysts were synthesized using deposition method. Definite quantities of the aqueous solutions of the corresponding metal salts $MnSO_4 \cdot H_2O$ or $CuSO_4 \cdot 5H_2O$ were used. The samples were finally calcined at 400 °C for 3 h in air.

Chemical composition of the samples was determined using Atomic Absorption Analysis FAAS - SOLAAR M5 spectrometer.

The X-ray diffraction (XRD) analysis was carried out on a Siemens powder diffractometer model D500 using $CuK\alpha$ radiation within a 2θ angle of diffraction interval of 10 ÷ 60 degrees. The identification of the phases was done by means of the JCPDS database of the International Center of Powder Diffraction Data. The particle size was determined by Scherrer's formula.

The determination of the specific surface area of the samples was carried out by nitrogen adsorption at the boiling temperature of liquid nitrogen (77.4 K) using a conventional volume measuring apparatus.

The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG Escalab II electron spectrometer using $AlK\alpha$ radiation with energy of 1486.6 eV under base pressure 10^{-7} Pa and a total instrumental resolution 1eV. The binding energies (BE) were determined utilizing the C1s line (from an adventitious carbon) as a reference with energy of 285.0 eV. The accuracy of the measured BE was 0.2 eV. The C1s, Zn2p, O1s, Mn2p and Cu2p photoelectron lines were recorded and corrected by subtracting a Shirley-type background and quantified using the peak area and Scofield's photoionization cross-sections.

The catalytic activity of the samples was studied in an isothermal plug flow reactor enabling operation under steady-state conditions without temperature gradients.

The size of the catalyst particles (0.3 ÷ 0.6 mm) was chosen taking into account the reactor diameter (6.0 mm) and the hourly space velocity ($20\ 000\ h^{-1}$) in order to reduce diffusion effects. The gas feed flow rate was 4.4 l/h, the catalyst bed volume was 0.2 cm³ and the mass of the catalyst charge was 0.5 ÷ 0.6 g. The catalytic oxidation of CO was performed at the temperature interval 200 ÷ 400 °C, the oxidizing agent used being oxygen from air (gas mixture: 21% O₂ and 79% N₂). The preliminary treatment of the catalyst included heating in air flow at 120 °C for 1 hour. The flow of CO was fed into the reactor by an Ismatex M62/6 pump (Switzerland).

The initial concentration of CO was 0.5 vol.%. The carrier gas was air (a mixture of 21% O₂ and 79% N₂). A Maihak (O₂/CO/CO₂) gas analyser was used to measure the CO and CO₂ concentrations with an accuracy of ±0.1 ppm, while the oxygen measurement accuracy was ±100 ppm.

RESULTS AND DISCUSSION

It is of interest to establish and to compare catalytic activity of doped with Mn and Cu zinc oxide. MnZnO and CuZnO catalysts obtained from carbonate, acetate and nitrate precursors as well as from doped pre-activated ZnO have been obtained and investigated. The values of specific surface areas of compounds obtained from different precursor are shown in Table 1.

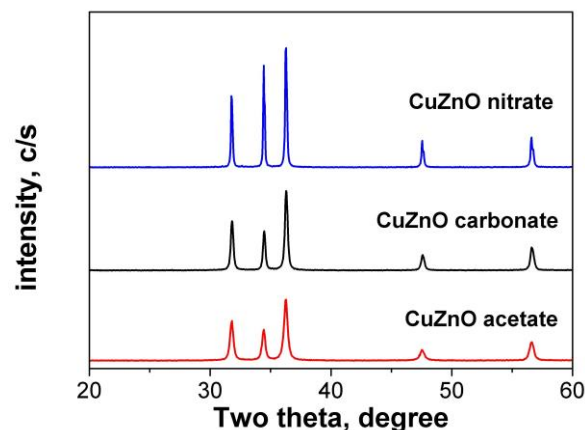
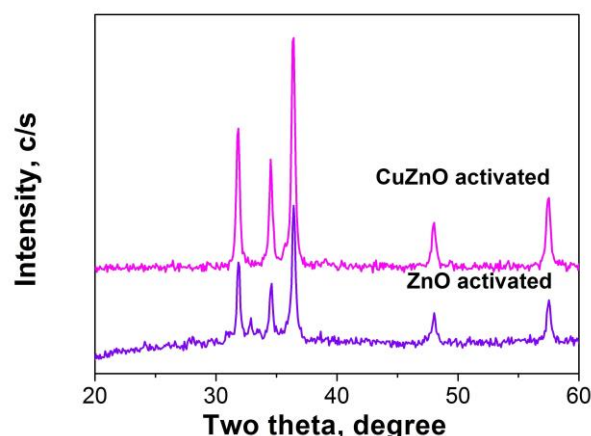
Table 1. Dopant content, crystallites size and specific surface area (A_{BET}) of Mn-doped and Cu-doped ZnO.

Sample	Dopant content, Wt.%	Crystallites size, nm	A_{BET} , m^2/g
MnZnO acetate	0.16	39	9
CuZnO acetate	0.19	36	10
MnZnO nitrate	0.14	68	1
CuZnO nitrate	0.17	57	1
MnZnO carbonate	0.15	31	23
CuZnO carbonate	0.18	27	23
CuZnO deposition	0.15	25	24
ZnO activated	-	25	44

It is evident that the specific surface area highly depends on the kind of used precursor, and from the doped element and the doping process, and also from the pre-activation of the obtained ZnO. That was expected, because the precursor decomposition also depends on their chemical composition. Lowest value of the specific surface area ($1 \text{ m}^2/\text{g}$) was measured for MnZnO nitrate and CuZnO nitrate samples. Possible explanation is the fact that the decomposition process passes in molten state. The samples obtained from carbonate precursor have the highest value of the specific area. All samples obtained have nanoscale sizes. Most fine crystals are observed for samples, obtained from basic zinc carbonate. It was observed tendency that Cu doping leads to lower sizes of oxide crystallites compared to Mn doping. XRD analysis of oxide samples (Figs. 1 and 2) show formation of hexagonal wurzite structure of ZnO (JCPDS 36-1451) observed for all samples. Diffractograms show only existence of ZnO phase, due to low content of the dopants Cu and Mn in it [18]. Probably the dopants are included in the lattice of ZnO leading to differences in the nanosize scale. The peak intensity is in correlation with investigated specific surface area. The width of diffraction lines also increases in the row: nitrate < acetate < carbonate in accordance with their specific area and the crystallinity. The obtained results correlate with the parameters of the precursor of ZnO.

XPS spectroscopy analysis of CuZnO and MnZnO samples was carried out. Fig. 3 and Fig. 4 present the observed Zn2p, O1s, Cu2p and Mn2p

lines. The results from investigation of Cao *et al.* of ZnO films doped with 1.5 wt.% Al and 0.2 wt.% Mn, shows that Mn^{2+} induce formation of more oxygen vacancies and this has been verified by O 1s XPS results [19].

**Fig. 1.** X-ray diffractograms of CuZnO carbonate, CuZnO acetate and CuZnO nitrate samples.**Fig. 2.** X-ray diffractograms of CuZnO activated and activated pure ZnO samples.

From XPS results was made estimation of manganese and copper contents and their chemical states, as Cu^{1+} and Mn^{2+} . The O1s peaks of Figs. 3 and 4 can be deconvoluted into three peaks corresponding to the low binding energy (LP), middle binding energy (MP), and high binding energy (HP) components centered at 530.30 ± 0.1 , 531.41 ± 0.11 , and 532.45 ± 0.05 eV, respectively. The first one is attributed to O^{2-} ions surrounded by Zn in the ZnO compound system. This peak is the indication of the amount of oxygen atoms in a fully oxidized, stoichiometric environment [20]. The middle peak centered at around 531.5 eV can be associated with the existence of O^x ions where $x < 2$ in the oxygen deficient region in the ZnO matrix and is related to the presence of oxygen vacancies [21].

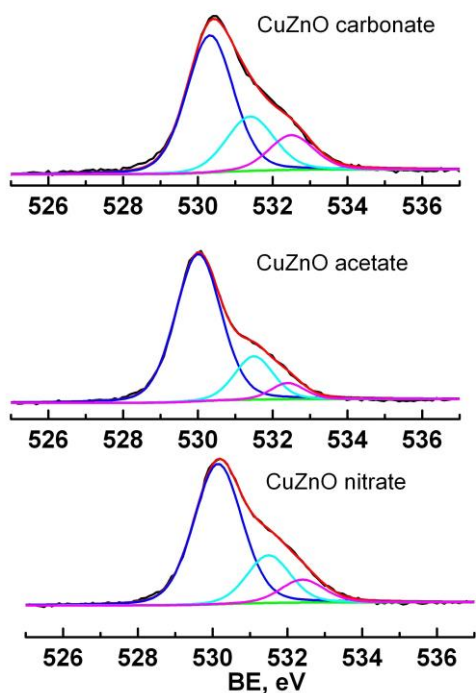


Fig. 3. XPS spectra of O1s for CuZnO samples obtained from nitrate, carbonate and acetate precursors.

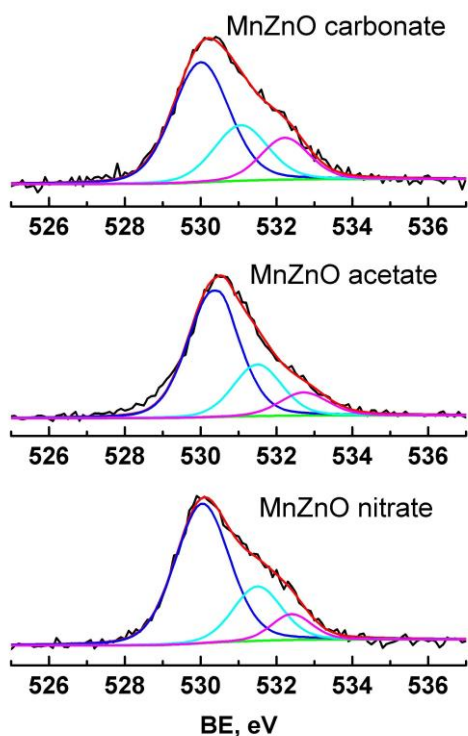


Fig. 4. XPS spectra of O1s for MnZnO samples obtained from nitrate, carbonate and acetate precursors.

The last higher binding energy peak is related to chemisorbed oxygen, dissociated oxygen, or OH⁻ groups on the surface. The area ratio of MP/(LP+MP+HP) for all investigated samples was

calculated. The MP/(LP+MP+HP) ratio for MnZnO samples is higher for the MnZnO (acetate), equal to 0.32, while the higher value for the CuZnO samples was evaluated for the CuZnO (carbonate), equal to 0.24. Obviously the higher the concentration of Cu and Mn atoms on the surface of the studied samples the higher the number of oxygen vacancies in them are. It is worth to notice here that the presence of Mn²⁺ into the ZnO introduce more oxygen vacancies than Cu⁺ into the ZnO independently of the used precursors.

The XPS investigation on Mn and Cu doped previously activated ZnO have been done too. The obtained and fitted results of the O1s photoelectron line are shown in Fig. 5. The area ratios of MP/(LP+MP+HP) for both samples have been calculated and were evaluated to be 0.29 for the Mn doped and 0.33 for the Cu doped one. The intensity of the HP and MP peak are almost equal, which indicates coexistence of oxygen vacancies and chemisorbed oxygen. The obtained result shows that the advanced procedure of activation ZnO is most probably due to the transfer of the oxygen atoms, oxygen vacancies and chemisorbed oxygen come forth simultaneously as dominant defects.

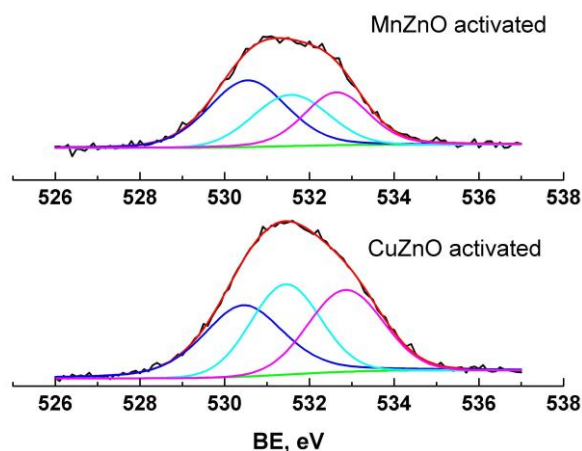


Fig. 5. XPS spectra of O1s for investigated samples after advanced activation of ZnO obtained from carbonate precursors.

The catalytic activity of CO oxidation reaction for different MnZnO and CuZnO samples is shown in Figs. 6a and 6b. The composition of the model gas used in the investigation is similar to those of the gases emitted by the automotive transport. Regarding CO oxidation it can be concluded, that the precursor of zinc oxide carrier is of great importance and the observed catalytic activity is in the row: carbonate > nitrate > acetate. It was also found that copper doping has better performance than manganese one when compare the samples

from the same precursor [22]. For the doped activated ZnO regardless of the kind of the dopant is observed higher activity in comparison with all other samples. Doping with Cu leads to 50% conversion at 290 °C, and full conversion is observed at about 330 °C. Doping with Mn of activated ZnO sample has lower effect over catalytic activity, respectively the temperatures for conversion are shifted to higher values - at temperatures between 360 °C and 370 °C a full conversion is achieved.

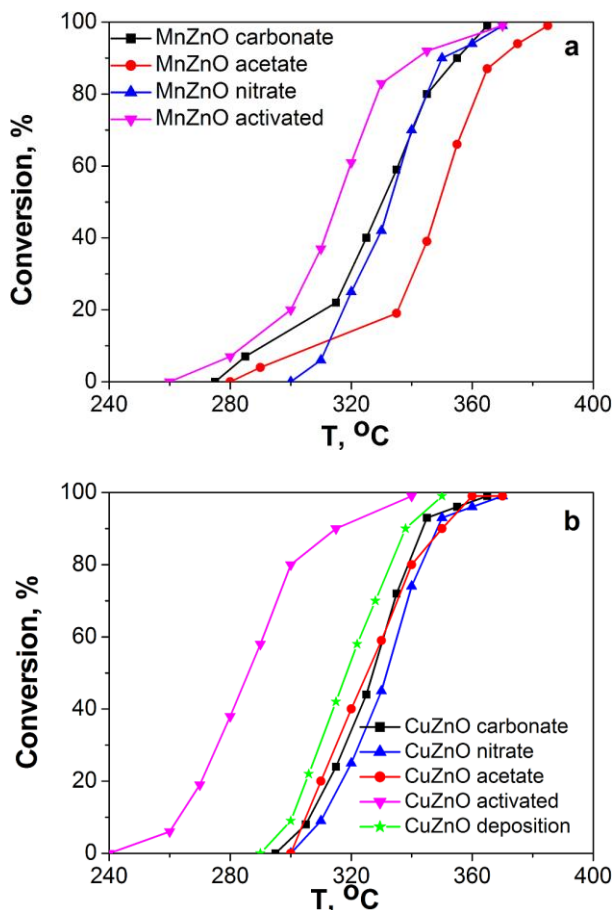


Fig. 6. Conversion of CO transformed to CO₂ of: a) MnZnO samples and b) CuZnO samples.

CONCLUSION

ZnO based catalysts doped with Cu and Mn (up to 0.2 wt.%) were synthesized from three different precursor solutions and the measured catalytic activity for CO oxidation reaction in waste gas emissions is ranged in the row: carbonate > acetate > nitrate. The presence of Cu as a dopant in catalytic compositions irrespective of used zinc oxide precursor provides higher catalytic activity toward investigated reaction. Activated zinc oxide

doped with Cu provides full conversion of CO at lowest temperature due to simultaneous role of oxygen vacancies and the oxygen absorbed on the surface of the catalyst. The obtained doped phases based on activated ZnO are perspective materials for industrial purification of gas fluids from CO.

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ДОТИРАНИ С Cu И Mn ЦИНКОВО ОКСИДНИ КАТАЛИЗАТОРИ ЗА ОКИСЛЕНИЕ НА CO ВЪВ ВРЕДНИ ГАЗОВИ ЕМИСИИ

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Постъпила на 30 януари 2017 г.; Коригирана на 16 февруари 2017 г.

(Резюме)

В настоящата работа дотиран с Cu и Mn цинков оксид е изследван като катализатор за окисление на CO. Дотираните проби от цинков оксид са получени от карбонатен, ацетатен и нитратен прекурсори и от активиран дотиран ZnO. Съдържанието на Mn и Cu в каталитичните композиции е под 1 wt %. За структурно, текстурно и морфологично охарактеризиране на пробите са използвани тривиални методи: Атомно Абсорбционна Спектроскопия (AAS), Рентгенофазов Дифракционен анализ (XRD), BET анализ на повърхността, Рентгенова Фотоелектронна Спектроскопия (XPS). Изследвана е и каталитичната активност. Съществува корелация между вида прекурсор, използван за синтеза на ZnO и каталитичното превръщане. Най-висока конверсия се наблюдава за Cu дотираната проба върху носител активиран ZnO: 50% конверсия при 290 °C и 95% при 320 °C. ZnO, синтезиран по стандартен метод от прекурсор карбонат претърпява 50% конверсия при около 35 °C по-висока температура, отколкото активираната проба. Резултатите от настоящото изследване показват висока перспектива на катализатори, получени от активирани карбонатни прекурсори.