

CO and VOCs oxidation over alumina supported Cu-Mn catalysts modified by cerium

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Catalytic oxidation is considered as one of the most promising and environment-friendly technologies for the abatement of CO and VOCs. The aim of this investigation was to study the effect of chemical composition, in particular the modification by cerium, on the activity and selectivity of the selected γ -alumina supported CuO-MnO₂ catalysts (Cu/Mn molar ratio 2:1 and 1: 5) in total oxidation of CO, dimethyl ether (DME) and methanol. The samples were characterized by BET, XRD, EPR and TPR. Structure-reactivity relationship was analyzed in order to explain the role of cerium.

Keywords: Copper-manganese-cerium catalyst, CO and VOCs oxidation.

INTRODUCTION

The study of lanthanides for various catalytic processes has been the subject of increasing interest over the past few decades [1, 2]. It is well known that CeO₂ is widely used as a promoter and/or carrier in many catalytic oxidation reactions, due to the facilitated redox transition Ce⁴⁺/Ce³⁺ and the high oxygen capacity [3]. Trovarelli [4] analysed in details the catalytic properties of CeO₂ and CeO₂-containing materials and concluded that some of the most important factors determining the suitability of CeO₂ for complete oxidation of volatile organic compounds are the reducing capability and high instability of oxygen in its lattice. The addition of cerium oxide to catalysts based on transition metals deposited on aluminum oxide may improve the ability to store oxygen [5] and the dispersion of the metal particles [6], to stabilize the carrier [4], to increase the rate of reaction of CO with water vapor through the water-gas shift reaction and to provide lattice oxygen for the oxidation of adsorbed reagents [7]. Other publications showed that cerium oxide can improve the activity in complete oxidation reactions not only over catalysts containing noble metals, but also over catalysts based on transition metals [8]. The advantage of the catalysts based on transition metal oxides as compared to catalysts based on noble metals is associated with the lower cost, but also with higher thermal stability and resistance to catalyst poisons, which is essential for their performance [9]. At low

temperatures, they are less active than the catalysts based on noble metals but certain specific combinations of metal oxides can lead to an improvement of the activity in the reactions for volatile organic compounds (VOCs) elimination [10]. Many authors have reported that the mixed metal oxides are more active in the oxidation of VOCs in comparison with the single-component oxides. It has been found that the combinations of MnO_x, Co₃O₄, CeO₂ and MnO_x-CeO₂, are just as active as deposited metal catalysts in the oxidation reaction of certain compounds [11]. The copper-containing catalysts for the elimination of CO from gaseous emissions are a subject of extensive studies in the scientific literature. Studies of Rao *et al.* [12] have shown that the oxide CuO-CeO₂ system is an effective catalyst in CO oxidation at low temperature due to the strong synergistic effect between the copper and CeO₂. Shi *et al.* [13] have studied CuO and the catalytic system based on CeO₂ for the reduction of CO, NO and C₃H₆. Their results showed that CuO, distributed in CeO₂/ γ -Al₂O₃, increases the thermal stability of catalysts. According to [14], the introduction of small amounts of CeO₂ in CuO_x leads to an increase in the dispersion of copper oxide.

The aim of present work was to study the modification of alumina supported mixed Cu-Mn oxides by introducing cerium and its effect on the activity and selectivity of the catalysts in total oxidation of CO, methanol, and dimethyl ether (DME).

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EXPERIMENTAL

Catalysts preparation

Copper-rich Cu-Mn/ γ -Al₂O₃ sample with Cu/Mn molar ratio 2:1 and manganese-rich sample with Cu/Mn molar ratio 1:5 were modified by replacing manganese by Ce in the whole concentration range from 0 to 100%. All catalysts were prepared by wet impregnation of γ -Al₂O₃ with fraction 0.6-1.0. Prior to the impregnation, the carrier was calcined for 2 hours at 450°C in a ceramic furnace. After keeping it at a room temperature, previously prepared solutions of copper, manganese and cerium nitrates were added. The support remained immersed for 12 hours in the salt solution at 80°C. After the impregnation samples were dried and calcined in the following sequence: 12 h drying at room temperature, followed by heating at 120°C for 10 h, after which the temperature was increased with 10°C/min up to 450°C and kept constant for 4 hours.

Sample characterization

Texture measurements. The texture characteristics were determined by low-temperature (-196°C) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e (USA) specific surface area&pore analyser. Pore diameter and total pore volume were determined in accordance with the Gurvich rule at a relative pressure close to 0.99, while the specific surface areas (S_{BET}) were estimated through the Brunauer, Emmett and Teller (BET) method in a standard pressure range $p/p_0=0.10-0.30$.

Powder X-ray diffraction (XRD). X-ray powder diffraction (XRD) patterns for phase identification were recorded on a Philips PW 1050 diffractometer, equipped with Cu K α tube and scintillation detector. Data for cell refinements were collected in θ -2 θ , step-scan mode in the angle interval from 10 to 90° (2 θ), at steps of 0.03° (2 θ) and counting time of 3 s/step. The cell refinements were obtained with the PowderCell program. The size-strain analysis was carried out using the BRASS-Bremen Rietveld Analysis and Structure Suite.

Temperature programmed reduction (TPR). Temperature-programmed reduction (TPR) of the samples was carried out in the measurement cell of

a differential scanning calorimeter model DSC-111 (SETARAM) directly connected to a gas chromatograph. The measurements were performed in the 30–650°C range at 15°C/min heating rate in flow of 10% H₂/Ar, the total flow rate being 25 ml/min, sample amount 0,05g.

Electron paramagnetic resonance (EPR). The EPR spectra were recorded at JEOL JES-FA 100 EPR spectrometer operating in X-band with standard TE₀₁₁ cylindrical resonator under following conditions: modulation frequency 100 kHz, microwave power 1 mW, modulation amplitude 0.2 mT, sweep 500 mT, time constant 0.3 s and sweeping time 4 min.

Catalyst testing. The catalytic measurements of CO, methanol and DME oxidation were carried out on continuous flow equipment with a four-channel isothermal stainless steel reactor, containing 1.0 ml catalyst at atmospheric pressure and space velocity (GHSV) of 10000 h⁻¹, allowing simultaneous examination of four catalysts under the same conditions. The flow of ambient air (40 – 50% humidity) and CO (final concentration 2.0%) were fed using mass flow controllers (GFC Mass Controller AABORG, Germany). Liquid methanol was cooled to 0°C in evaporator through which the stream of air was passing and additional air was added before reaching the preheater to final concentration of methanol 2.0%. DME (final concentration 0.8–1.0%) was obtained by dehydration of methanol in nitrogen flow on γ -Al₂O₃ in tubular isothermal reactor. Gas mixtures on the input and output of the reactor were analyzed with a gas chromatograph HP 5890 Series II, equipped with FID and TCD detectors, column Porapak Q (for methanol, CO₂ and DME) and column MS-5A (for CO, oxygen and nitrogen).

RESULTS AND DISCUSSIONS

Texture characteristics

Table 1 shows the specific surface area, pore volume and average pore diameter of the support, samples with Cu/Ce 2:1 и 1:5 and modified sample Cu/(Mn+Ce) 1:5, in which 20% manganese is replaced by Ce. It is seen that the specific surface of the modified sample increases compared to the basic one. The pore volume and average pore diameter of catalyst samples are nearly identical.

Table 1. Specific surface, pore volume and average pore diameter of selected catalyst.

| Composition | S_{BET} [m ² /g] | V_{total} [cm ³ /g] | $D_{\text{aver.}}$ [nm] |
|--------------------------------|---|--|----------------------------|
| Al ₂ O ₃ | 219 | 0.40 | 7.40 |
| Cu/Ce 2:1 | 156 | 0.29 | 7.30 |
| Cu/Ce 1:5 | 165 | 0.29 | 7.00 |
| Cu/(Mn+Ce) 1:5 20% Ce | 193 | 0.30 | 6.10 |

Powder X-ray diffraction (XRD)

The phase composition of the samples was analyzed on the basis of powder X-ray diffraction data. In Fig. 1 (a) are compared the XRD patterns of the catalysts with Cu:Mn molar ratio 2:1, in which manganese is replaced partially (20, 40, 60 and 80 %) or completely by cerium. The X-ray diffractogram of CeO₂/Al₂O₃ is also shown for comparison. The reflections typical for CuO at 2 θ = 35.6, 38.8, 48.6 and 61.8 (marked with *, JCPDS 02-1040) were observed in the X-ray diffractogram of the sample with Cu:Mn ratio 2:1. The

replacement of Mn by cerium led to decreased intensity of these peaks, due to partial amorphization of CuO phase. This phenomenon could be attributed to the formation of small CuO crystallites in agreement with well-known property of ceria to favor high dispersion of CuO particles. New peaks appeared at 2 θ = 28.5, 33.1, 47.5 and 56.3, related to fluorite oxide-type diffraction pattern of CeO₂ (marked with o, JCPDS 43-1002). These peaks are better discernible in the XRD pattern of Cu-Mn (60 and 80 wt.% Ce) due to the increased amount of separate phase of ceria.

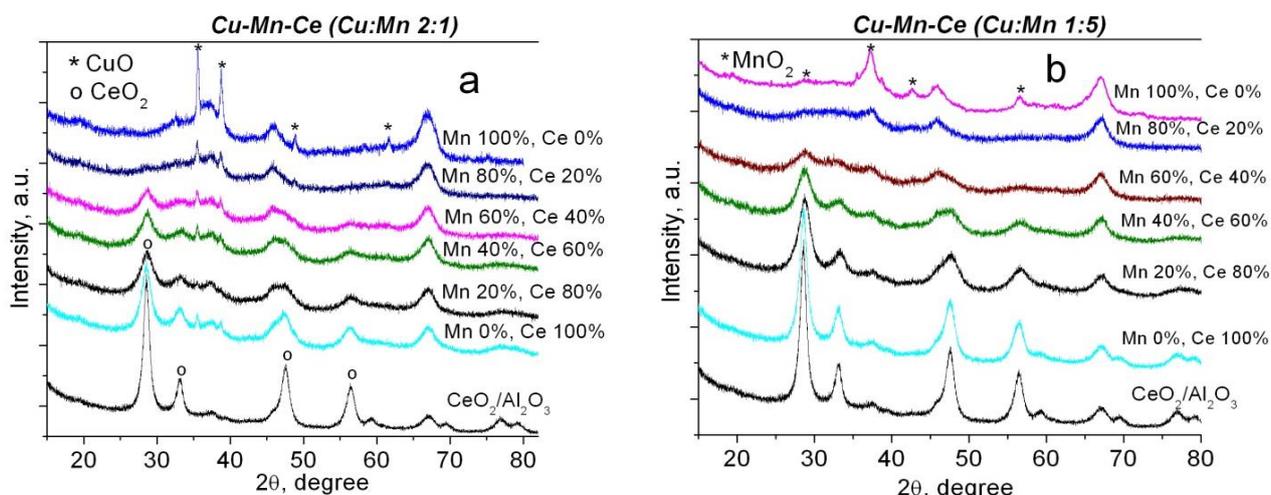


Fig. 1. XRD patterns of Cu-Mn-Ce catalysts with Cu/(Mn+Ce) molar ratio 2:1 (a) and 1:5 (b) after partial or total replacement of Mn by Ce.

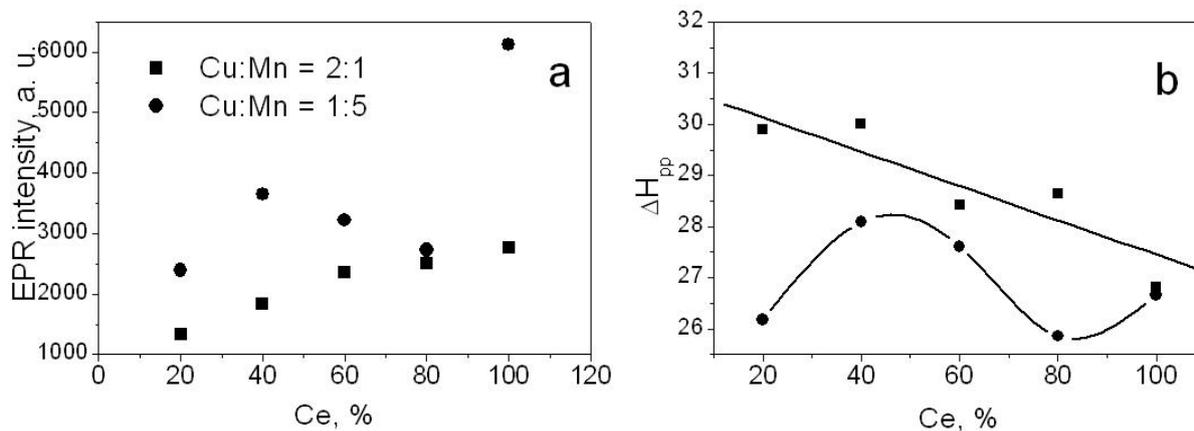


Fig. 2. EPR spectra intensity (a) and line width (b) of Cu-Mn-Ce catalysts with Cu/(Mn+Ce) molar ratio 2:1 (squares) and 1:5 (circles) depending on the content of Ce.

The XRD patterns of alumina supported catalysts with Cu:Mn molar ratio 1:5 after partial or total substitution of Mn by Ce are shown in Fig. 1 (b). Similarly to the observed above differences, the intensity of the reflections of MnO₂ at 2 θ = 28.6, 37.2, 42.8 and 56.5 (marked with *, JCPDS 24-0735) decreased upon replacement of Mn by Ce.

Obviously, the presence of separate phase of ceria was beneficial for dispersion of MnO₂.

Electron paramagnetic resonance (EPR)

Experimental evidences for the role of cerium on the structural features of all samples were provided by EPR spectroscopic study. The EPR spectra of Cu-Mn/ γ -Al₂O₃ samples with Cu/Mn

molar ratio of 2:1 and 1:5 with spectral parameters $g_{\parallel} = 2.3572$ and $g_{\perp} = 2.1025$ (not shown) were interpreted as arising from the distorted octahedrally coordinated Cu^{2+} ions. The four-line hyperfine splittings indicated presence of isolated Cu^{2+} ions ($I=3/2$) on the γ -alumina surface. In Fig. 2 (a) is shown the dependence of the EPR spectrum intensity on the content of Ce. The results clearly demonstrated that the effect of cerium was closely related to Cu:Mn molar ratio. A gradual increase of the spectrum intensity due to higher content of cerium was observed for copper-rich Cu-Mn/ γ - Al_2O_3 samples with Cu/Mn molar ratio of 2:1 (square symbol). This result indicated that the replacement of Mn with higher amount Ce was favorable for increasing of the number of isolated Cu^{2+} ions. Isolated Cu^{2+} ions can strongly interact with the support because they have no spin-spin interaction. This finding is in agreement with the tendency of decreasing EPR line width (Fig. 2, b) and could be related to improved distribution of

isolated Cu^{2+} ions in octahedral coordination with tetragonal distortion. The lack of dipole-dipole interaction may be considered as evidence for better dispersion of CuO in the presence of higher amount CeO_2 . This suggestion agrees well with analysis of XRD data.

In the case of manganese-rich Cu-Mn/ γ - Al_2O_3 samples with Cu/Mn molar ratio of 1:5, both dependences (Fig. 2 and b, circle symbols) passed through a maximum at 40 % Ce and a minimum at 80 % Ce. The relationship between catalytic activity and Ce content followed similar trend (Fig. 10). Considering higher amount of Mn in the samples with Cu/Mn molar ratio 1:5, it could be hypothesized that these complex dependences are related to the changes in the oxidation state of Mn. Another reason could be the dipolar coupling arising from the strong interaction of near-neighbor copper atoms and formation of clusters possessing antiferromagnetic couplings, which make them undetectable by EPR.

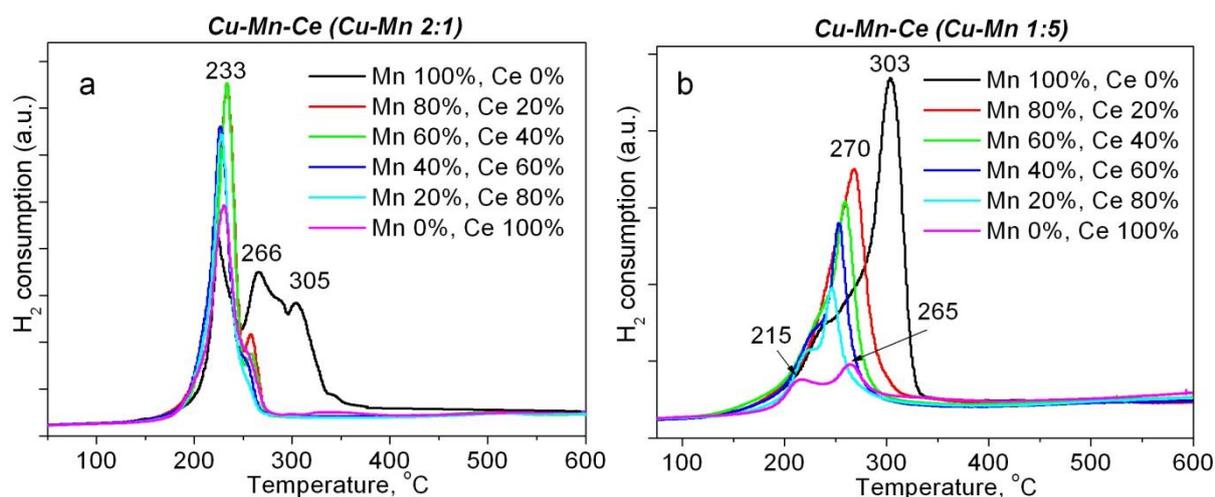


Fig. 3. TPR profiles of Cu-Mn-Ce catalysts with Cu/(Mn+Ce) molar ratio 2:1 (a) and 1:5 (b) after partial or total replacement of Mn by Ce.

Temperature programmed reduction (TPR)

The H_2 -TPR was used to study the reducibility of the catalysts. As can be seen in Fig. 3, the TPR profiles are complex due to the reduction of CuO or MnO_2 in addition to that of surface oxygen of ceria. The complex TPR profile of Cu-Mn with ratio 2:1 (black curve in section a) may be assigned to the reduction of separate CuO phase ($T_{\max} 230^\circ\text{C}$), highly dispersed Cu-Mn spinel phase ($T_{\max} 266^\circ\text{C}$) and some transition of Mn^{4+} to Mn^{3+} . The peak with well-defined maximum at 303°C in the profile of Cu-Mn with ratio 1:5 (black curve in section b) should be ascribed to reduction of MnO_2 , while a

broad shoulder at the low-temperature side of the profile could be related to the reduction of CuO .

The analysis of TPR profiles of alumina supported Cu-Mn-Ce samples indicated that the reduction behavior was affected by the presence of separate ceria phase. It is known from the literature that H_2 -TRP profile of ceria contains two major peaks, one at lower temperature (around 500°C), assigned to the reduction of surface oxygen, and one at higher temperature (around 800°C), attributed to the removal of bulk oxygen from the ceria structure [14]. Many authors have shown that some transition metals (Cu, Ni) [15] promote the surface reduction of Ce^{4+} to Ce^{3+} . The first reduction peak can be shifted to much lower

temperature, while the high-reduction peak remains unchanged.

The general finding in this work was the decreased hydrogen consumption in the samples containing Ce. However, it should be considered that the theoretical values of hydrogen consumption for ceria surface layers reduction (which is of interest in present case) according to literature data is limited to 17 % [16] or 20 % [17]. Stronger effect on samples reducibility due to replacement of Mn by Ce was observed for Cu-Mn-Ce samples with Cu/Mn molar ratio of 1:5. A significant shift of T_{max} to lower temperature was registered with increase of Ce content. The complex shape with two maxima in the profile of sample with 100% Ce (pink curve) could be explained with reduction of CuO (T_{max} 215°C) and ceria surface oxygen (T_{max} 265°C).

The results for CO, methanol and DME oxidation over Cu-Mn-Ce/ γ -Al₂O₃ catalyst with molar ratio Cu/(Mn+Ce) 2:1 and 1:5, in which Mn is replaced by Ce in the whole concentration range from 0 to 100%, are presented in Figs. 4-7. The results, presented in Fig. 4 (a) indicated that the catalytic activity of the samples with molar ratio Cu/(Mn+Ce) 2:1 varied significantly at the whole temperature range depending on the catalysts composition. There is a clear trend of increased activity by increasing the content of cerium. The oxidation reaction started above 80°C, while on the all mixed Cu-Mn-Ce/ γ -Al₂O₃ samples complete CO oxidation was achieved in the temperature range 180 - 200°C. For nonmodified Cu-Mn/ γ -Al₂O₃ catalyst this temperature was 200°C and for sample with total replacement of Mn, i.e. Cu-Ce/ γ -Al₂O₃ - significantly lower (160°C).

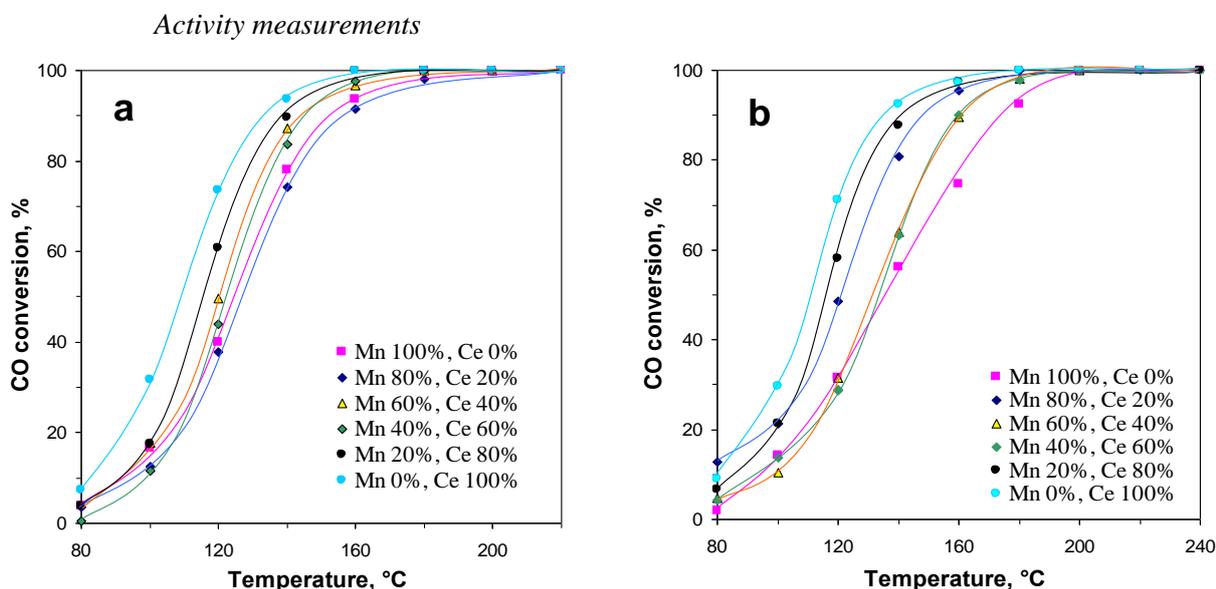


Fig. 4. Temperature dependence of CO oxidation over Cu-Mn-Ce/ γ -Al₂O₃ catalyst with Cu/(Mn+Ce) molar ratio 2:1 (a) and over Cu-Mn-Ce/ γ -Al₂O₃ catalyst with Cu/(Mn+Ce) molar ratio 1:5 (b).

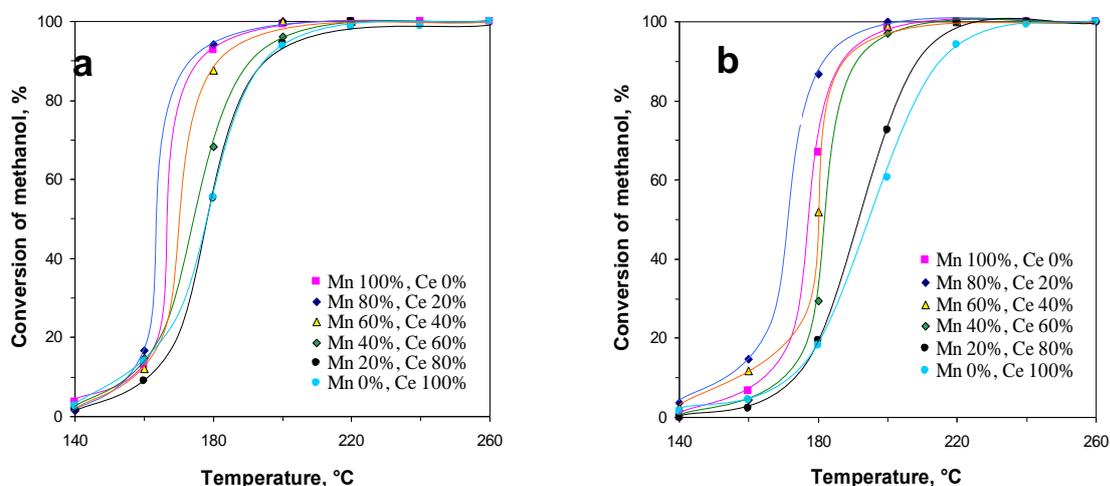


Fig. 5. Temperature dependence of methanol oxidation over Cu-Mn-Ce/ γ -Al₂O₃ catalyst with Cu/(Mn+Ce) molar ratio 2:1 (a) and Cu-Mn-Ce/ γ -Al₂O₃ catalyst with Cu/(Mn+Ce) molar ratio 1:5 (b).

The trend in the CO oxidation (Fig. 4, b) over the samples with molar ratio Cu/(Mn+Ce) 1:5 is similar to those represented in Fig. 4 (a). The samples with a high content of cerium showed high catalytic activity, while Cu-Mn/ γ -Al₂O₃ exhibited the lowest activity.

The oxidation of methanol (Fig. 5 a and b) over all samples started at 140°C and complete oxidation was reached at 220 - 240°C, observing the opposite tendency than in CO oxidation. In this case the

most active were the manganese-rich Cu-Mn/ γ -Al₂O₃ samples and the lowest activity demonstrated Cu-Ce/ γ -Al₂O₃.

The oxidation of DME (Fig. 6 a, b) began at 220°C, and complete oxidation was attained at about 360°C except for the samples, containing a large amount of Ce (Mn20%/Ce80% and Ce100%). Unlike of CO and methanol oxidation, the best performance for DME oxidation was demonstrated by the sample modified with 20% Ce.

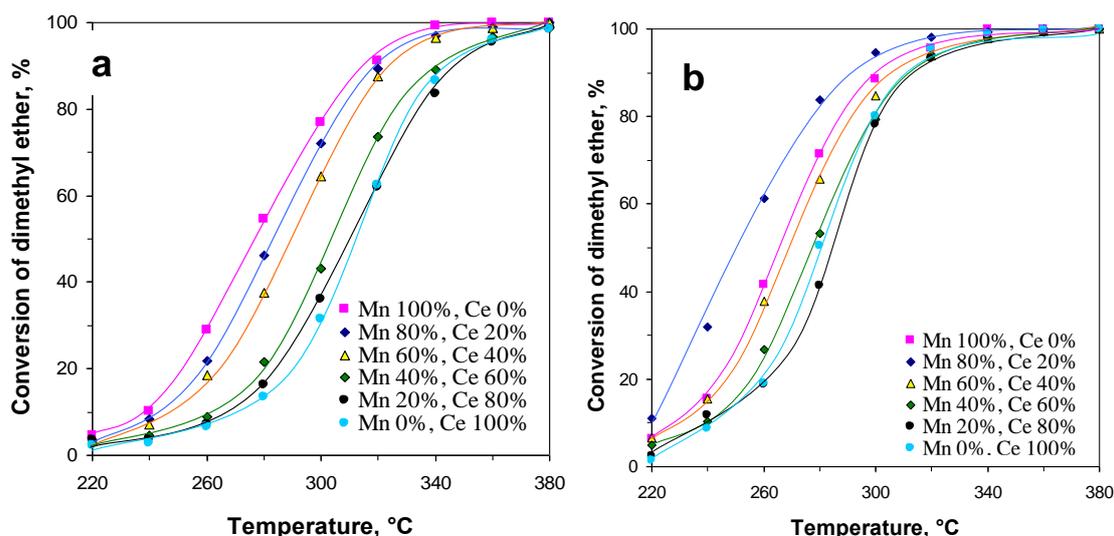


Fig. 6. Temperature dependence of DME oxidation over Cu-Mn-Ce/ γ -Al₂O₃ catalyst with Cu/(Mn+Ce) molar ratio 2:1 (a) and Cu-Mn-Ce/ γ -Al₂O₃ catalyst with Cu/(Mn+Ce) molar ratio 1:5 (b).

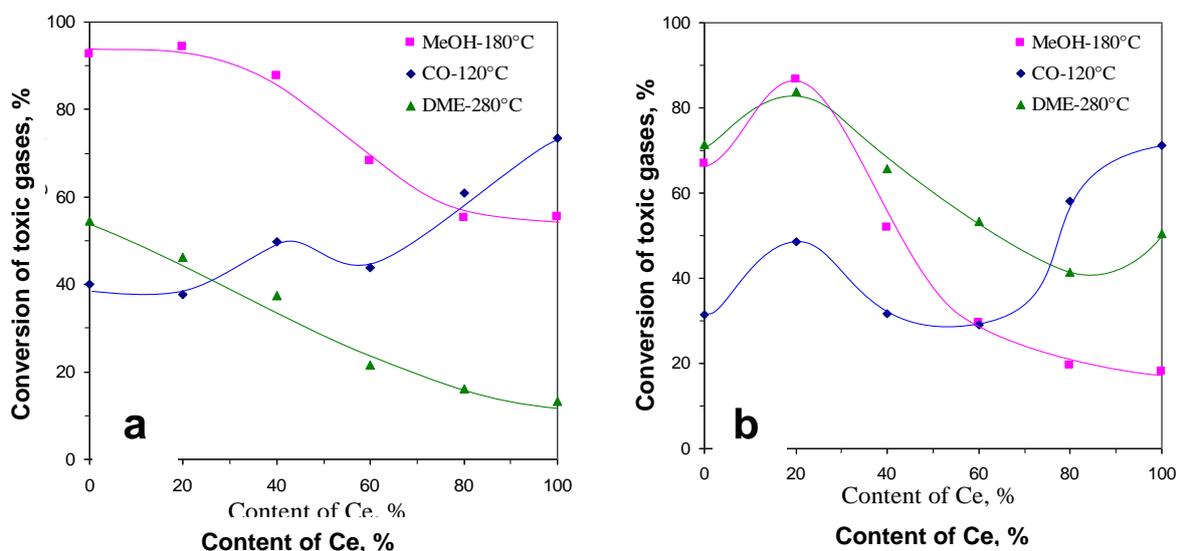


Fig. 7. Effect of ceria amount in the active component of Cu-Mn-Ce/ γ -Al₂O₃ catalysts with a molar ratio Cu/(Mn + Ce) 2:1 (a) and 1:5 (b) on CO, CH₃OH and DME oxidation ($T_{CO} = 120$ °C, $T_{MeOH} = 180$ °C, $T_{DME} = 280$ °C).

For easier interpretation of the results and assessment of the impact of manganese substitution

by cerium in the mixed Cu-Mn-Ce catalysts, part of the data are summarized in Figs. 7.

The results showed a general trend of increasing activity in CO oxidation and decreasing activity in methanol and DME oxidation with the increase of cerium content for both groups of catalyst. This general trend, however, contains specific features, depending on the composition of the catalyst and the type of the oxidized compound. The samples composed predominantly of copper (Cu/Mn molar ratio 2:1) exhibited increased degree of CO oxidation in the whole concentration region. This performance could be attributed to the formation of smaller CuO crystallites in the presence of ceria, in accordance with XRD and EPR results. Additionally, it should be considered the ability of ceria to provide active oxygen species via Mars–van Krevelen mechanism. As concerns the manganese-rich samples (Cu/Mn molar ratio 1:5) the slope of the curve is a little bit different and catalysts behavior should be related to very complex composition of these materials. Indeed, in XRD pattern of the sample Cu/Mn with molar ratio 1:5 (Fig. 1 b, pink line) were clearly observed reflections due to the presence of MnO₂. Additionally, selected area of the image, obtained by TEM was carefully analyzed (not shown). The distances among the fringes were measured and the spacing of the fringes 0.293 and 0.250 nm closely corresponded to the (2 2 0) and (3 1 1) lattice plane of Cu_{1.5}Mn_{1.5}O₄. Partial replacement of Mn by Ce led to formation of new phase of ceria, but this process was accompanied with decreased amount of separate MnO₂ phase and probably with lower content of spinel phase. Our very recent results indicated that alumina supported single Cu and Mn oxide catalysts were less active than mixed ones and the synergistic effect between copper and manganese oxides played a key role for increased CO oxidation activity [18]. In the samples with gradual increased content of ceria obviously were available diverse amounts of MnO₂, Cu_{1.5}Mn_{1.5}O₄ and CeO₂ with different impact on the catalytic performance. The sample, in which Mn was totally replaced by Ce, exhibited more than twice higher degree of CO oxidation, indicating that the synergism between copper and cerium is more favourable for CO oxidation, than in the case of Cu and Mn.

With respect to methanol oxidation, the trends are in the reverse direction. The replacement of manganese with cerium led to decrease in the activity, more significant pronounced for the copper-rich samples.

In the case of copper-rich samples, the activity decreased insignificantly up to 40 % manganese replacement by Ce and further increase of Ce

content caused gradual loss of about 30 % degree of CH₃OH conversion. In contrast to the performance in CO oxidation, the increased amount of separate CeO₂ phase does not contributed for better CH₃OH oxidation activity. Although XRD and EPR results revealed better dispersion of CuO in the samples with higher content of ceria, obviously the composition, i.e. twice higher amount of CuO is not beneficial for the catalytic performance. The activity of manganese-rich catalysts passed through a maximum at 20 % Mn replacement by Ce, after which followed rapid decrease. This is in agreement with EPR results, showing formation of CuO clusters and decreasing the number of the isolated Cu²⁺ ions in the presence of CeO₂.

The activity in the oxidation of DME followed the same tendency of decreasing with Mn replacement for both groups of catalysts and this is more pronounced for the copper-rich samples. The activity of the samples with Cu-Mn molar ratio 1:5 is much higher than that of the samples with Cu-Mn molar ratio 2:1. This behavior should be related to the substantial difference in the individual activity of copper and manganese toward DME oxidation, recently reported [18]. As in the cases of CO and methanol oxidation the replacement of small amount of manganese with cerium (to 20% Ce) led to an increase in activity of the samples with Cu/Mn molar ratio 1:5, after which the activity decreases significantly because of the reasons, described above.

The results for CO, methanol and DME oxidation can not be connected with the texture characteristics, presented in Table 1. Obviously, the catalysts composition is the decisive factor controlling the catalytic activity.

Summarizing the analysis of catalytic measurements data, it was found that the presence of separate phase of ceria affected positively mainly the CO oxidation activity. The interpretation of the relationship between composition and catalytic activity inferred the role of the reducibility on the different performance in oxidation of CO, CH₃OH and DME. The amount of consumed hydrogen during TPR measurements of all Ce-containing samples was lower than the one of alumina supported Cu-Mn samples. In a recent paper, the MeOH oxidation activity of these samples was correlated with better reducibility due to the presence of structural defects, in particular oxygen vacancies [18]. The availability of lower amount mobile lattice oxygen in the case of Cu-Mn-Ce samples could be the reason for observed trends in catalysts behavior.

CONCLUSIONS

The results presented showed that:

- The substitution of manganese by cerium in the mixed Cu-Mn-Ce/ γ -Al₂O₃ catalysts with molar ratio Cu/(Mn + Ce) 2:1 and 1:5 resulted in materials with very complex composition.
- The presences of a separate phase of ceria affected favorably the CO oxidation activity. This finding could be explained by the ability of ceria to take part in the oxidation reaction providing active oxygen species via Mars–van Krevelen

mechanism. The replacement of small amount of manganese with cerium (up to 20% Ce) was beneficial for an increase in CO, methanol and DME oxidation activity of the samples with Cu/Mn molar ratio 1:5.

The reducibility, i.e. mobility of lattice surface oxygen, influenced catalytic performance in methanol and DME oxidation.

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ОКИСЛЕНИЕ НА СО И ЛОС ВЪРХУ НАНЕСЕНИ НА АЛУМИНИЕВ ОКСИД Cu-Mn КАТАЛИЗАТОРИ, МОДИФИЦИРАНИ С ЦЕРИЙ

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(Резюме)

Каталитичното окисление се счита за една от най-обещаващите и екологично чисти технологии за намаляване съдържанието на СО и летливи органични съединения. Целта на това проучване е да се изследва ефекта на химичния състав, по точно модифицирането с церий, върху активността и селективността на нанесени върху γ -алуминиев оксид CuO-MnO₂ катализатори (молно съотношение Cu/Mn 2:1 и 1:5) по отношение на пълното окисление на СО, диметилов етер (DME) и метанол. Катализаторните образци са охарактеризирани с рентгеноструктурен анализ (XRD), текстурни изследвания, електронен парамагнитен резонанс (EPR) и температурно-програмирана редукция (TPR). Зависимостта между структурата и реактивоспособността на изследваните образци е анализирана с цел обяснение на ролята на добавката от церий.