Co-Mn mixed oxide catalysts for purification of waste gases from *n*-hexane

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Single-component Co and Mn and bi-component Co-Mn oxide samples have been prepared by precipitation, characterized by different methods (XRD, TPR and XPS) and tested in the reaction of complete *n*-hexane oxidation. The highest activity demonstrated the catalyst, with Co/Mn=1 molar ratio (CoMn1). The coexisting of pairs Co^{2+}-Co^{3+} and Mn^{3+}-Mn^{4+} with the predominance of Co^{3+} and Mn^{4+} species, high specific surface area and low degree of crystallinity are responsible for highest catalytic activity of the CoMn1 sample.

INTRODUCTION

Air pollution has been one of the European Union's main environmental policy concerns since the late 1970s [1]. In 2013, the EU proposed a Clean Air Policy Package to reduce future emissions of air pollutants until 2030. The main air pollutants are particulate matter (PM), SO_2, NH_3, NOx, volatile organic compounds (VOCs), CH_4. Abatement of volatile organic compounds (VOCs) and carbon monoxide (CO) in the waste gases is an important task in regard to environmental protection and odour control. Such gaseous emissions are discharged by many branches of industry, such as chemistry and petrochemistry, oil and natural gas processing, energy production, machinery, polygraphy, food processing and many others. VOCs are involved in the formation of ground level ozone, ozone depletion and some of them can act as greenhouse gases [2, 3]. There are many techniques for VOCs removal, such as adsorption, absorption, biofiltration, thermal, and catalytic combustion [4, 5]. The choice of the technique to be used depends on the VOC nature, its concentration and waste gas flow rate. The catalytic combustion is a promising abatement technique for VOCs removal especially in cases when the organics cannot be recycled or it is present in low concentrations [6]. Since the catalytic combustion takes place at temperatures much lower than those required for thermal incineration, it results in lower costs and low NOx formation. Moreover, the efficiency of VOCs catalytic combustion is higher than that of thermal incineration. There are a great number of successful commercial catalysts developed for CO and VOC total oxidation. It is well known that the catalysts for CO oxidation and VOC combustion can be classified into three categories: supported noble metals, metal oxides or supported metal oxides, mixtures of noble metal and metal oxides. The major part of the commercial catalysts for these processes belongs to the first category, because the reaction can start at temperature as low as the room temperature. Nevertheless, there still exists a demand for development of new optimized catalysts with increased efficiency for mass and heat transfer [7, 8] and which do not contain any noble metals. The high cost of precious metals, their limited availability and sensitivity to higher temperatures and poisons has motivated the search for substitute catalysts. Among all the studied metal oxides the most active single metal oxides are those of Cu, Co, Mn and Ni [9]. Manganese and cobalt containing catalysts are less expensive and they demonstrate high activity in CO and VOCs oxidation [10, 11]. Despite the large number of studies on single component manganese oxides [12, 13] and cobalt oxide [14-17] based catalysts, there are only a few works focused on the catalytic properties of combinations of these two oxides in the combustion reaction of VOCs [18]. According to literature data the addition of manganese to the cobalt catalysts results in decrease of the Co_3O_4 particles size [19] and it also facilitates their reduction. In our previous studies [20, 21] we established that the combination between cobalt and manganese oxides changed significantly the activity in the *n*-hexane and methane oxidation and this depended on the sequence of cobalt/ manganese introduction.

The current work is orientated towards investigation of structural and catalytic properties of a series of cobalt-manganese mixed oxides. The test reaction is *n*-hexane combustion. *n*-Hexane is one of the major air pollutants being component of many emissions and effluents related to industry.

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EXPERIMENTAL

Catalyst preparation

The catalyst samples were prepared using a co-precipitation procedure. Aqueous solutions of $Co(NO_3)_2.6H_2O$ and $Mn(NO_3)_2.4H_2O$ with different molar ratios were premixed. The single component cobalt and manganese samples were also prepared. Aqueous solution of Na_2CO_3 (1 mol/l) was added slowly to the mixed nitrate solution at continuous stirring and maintaining the temperature of 70 ºC. The final pH value was 11. The precipitate was filtered and then washed several times with distilled water until reaching pH = 7. The product was then dried at 60 ºC and subsequently calcined at 500 ºC for 3 hours. The samples were denoted as Co, Mn, CoMn1.5, CoMn1, and CoMn3 where the number represents the Mn/Co bulk ratio.

Catalysis characterization

The specific surface area of the catalyst samples was determined by low temperature adsorption of nitrogen according to the BET method using a Nova 1200 (Quantachrome) apparatus. Prior to each measurement, the samples were degassed for 3 hours at 300 °C.

X-ray diffraction (XRD) patterns were recorded on TUR M62 apparatus, HZG-4 goniometer with Bregg-Brentano geometry, CoKα radiation and Fe filter. XRD data processing was performed by using the X'Pert HighScore program.

Temperature programmed reduction (TPR) was carried out feeding a flow mixture of 10 % H_2 in Ar at 10 ml/min flow rate, temperature rate of 10 °C/min up to 700 °C.

The cobalt and manganese concentrations in the catalysts were determined by Atomic absorption spectroscopy (AAS) using Perkin Elmer 5000 spectrophotometer and Inductively coupled plasma - Atomic emission spectroscopy (ICP-AES) performed by High Dispersion ICP-OES Prodigy spectrometer. The results are an average value of three parallel measurements. The measurement accuracy is 0.02% (relative standard deviation).

X-ray photoelectron spectroscopy (XPS) measurements were carried out on the ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5×10^{-10} mbar using twin anode MgKα/AlKα X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. The spectra were recorded at the total instrumental resolution (as it was measured at the FWHM of $Ag3d_{5/2}$ photoelectron line) of 1.06 and 1.18 eV for MgKα and AlKα excitation sources, respectively. The energy scale has been calibrated by normalizing the C1s line of adsorbed adventitious hydrocarbons to 285.0 eV. The processing of the

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measured spectra includes a subtraction of X-ray satellites and Shirley's type of background [22]. The peak positions and areas are evaluated by a symmetrical Gaussian-Lorentzian curve fitting. The relative concentrations of the different chemical species are determined based on normalization of the peak areas to their photoionization cross-sections, calculated by Scofield [23].

Catalytic measurements

n-Hexane oxidation was carried out in a continuous flow type of glass reactor at atmospheric pressure with catalyst bed volume of about 1 cm^3 (fraction 0.31–0.63 mm). External mass transfer limitations have been minimized by working at high gaseous hourly space velocity GHSV (14400 h^{-1}). The reaction temperature was measured by internal thermocouple. The concentration of *n*-hexane in air at the reactor inlet was fixed at 830 ppm. The reaction products were analysed by a HP5890 gas chromatograph equipped with thermal conductivity detector and flame ionization detector. "Aalborg" mass flow controllers were used to maintain stable gas flow rates. The gas chromatograph was calibrated based on known concentrations of *n*-hexane and the decrease in the respective peak areas was used as a measure of the conversion degree. The conversion degree was calculated as the ratio of converted to inlet quantity of hexane.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the calcined single- and bi- component samples are shown in Figure 1. The main phase in the single component Co catalyst is Co_3O_4 determined by the peaks at (2θ = 21.90, 36.77, 43.19, 44.95, 52.58, 65.69, 70.28, 77.49, and 92.98) (PDF 01-074-1657). The manganese sample (Mn) exhibited diffraction lines corresponding to Mn_2O_3 (2θ = 27.87, 38.34, 44.62, 65.66, 73.9) (PDF = 01-078-0390), Mn_3O_4 (2θ = 21.01, 37.10, 44.67, 56.07) (PDF = 00-016-0350) and MnO_2 (2θ = 33.20, 65.17) (PDF 00-004-0591). The diffraction reflections appear at slightly smaller 2θ values in the Co-Mn mixed samples. This is direct proof for the incorporation of manganese in the lattice of Co_3O_4. As it is known Co and Mn cations have similar ionic radii and can form stable mixed oxides members of solid-solution series [20]. The XRD reflections for $CoMnO_3$ (2θ = 28.4, 38.5, 63.8) (PDF-00-012-0476) are visible in the spectrum of CoMn3 sample. The diffraction peaks for all bi-component samples are weak and relatively broad making difficult the phase identification. On the other hand this is an evidence for high dispersity of prepared mixed oxide materials.

Table 1 presents the results of samples characterization by N_2 adsorption, elemental analysis, and XPS.

Pure cobalt and manganese oxides have comparable surface areas while that of the bicomponent is higher. One of possible explanation is that the nano-size oxide formation is responsible for increasing in surface area. It can be seen from the table that by increasing the amount of manganese, the surface area gradually decreases.

The oxidation state of cobalt and manganese on the surface is determined by XPS analysis. Figure 2 shows the spectra in the regions of $Co2p_{1/2}$ and Mn2p. The presence of Co^{2+} ions in the cobalt-containing samples is confirmed by the presence of a peak with binding energy 796.9 eV, together with the relatively intensive 3d→4s "shake-up" satellite with binding energy 803-804 eV (Figure 2A). The presence of Co^{2+} and Co^{3+} ions is observed in all Co-contained samples (see Table 1).

Figure 2B shows the XP spectra of manganese-containing samples in Mn2p region. Registered binding energies in the intervals 641.5 - 642.5 eV and 642.5 - 643.5 eV are characteristic of Mn^{3+} and Mn^{4+} ions, respectively.

From the spectra (Figure 2B) it is determined that the concentration of Mn^{4+}-containing species is higher than that of Mn^{3+} species.

As it can be seen from Table 1, the Co/Mn ratio in the bulk is higher than that on the surface demonstrating enrichment in manganese on the surface in the mixed samples with increasing its concentration in the sample. From the analysis of XPS data we found, also, that with increasing of the amount of manganese the relative abundance of Co^{3+} ions sharply decreases. According the authors in [9], the doping of manganese into the spinel structure of cobalt oxide increased crystal defects, which probably caused the increase of the amount of octahedrally coordinated divalent cobalt cations that are responsible for catalytic activity. As can be seen from the Table 1, Mn^{3+} and Mn^{4+} present simultaneously on the surface.

Table 1. Sample characterization

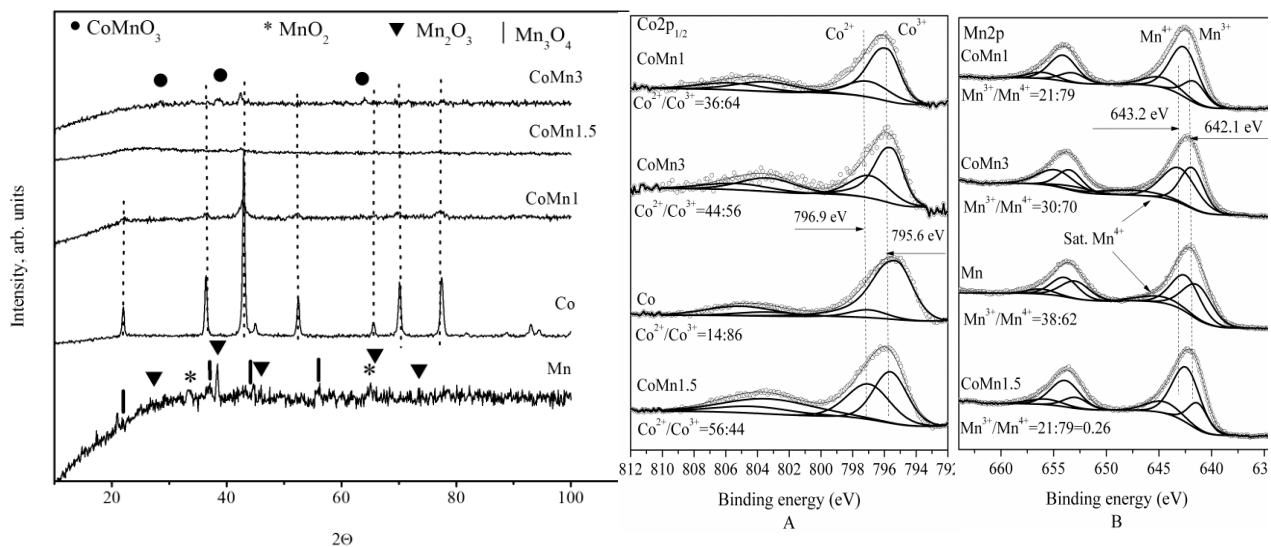| Sample	S_{BET}, [m²/g]	Co/Mn in the bulk (elemental analysis)	Co/Mn at the surface (XPS)	Co^{2+} [at.%]	Co^{3+} [at.%]	Mn^{3+} [at.%]	Mn^{4+} [at.%]
Co	26	-	-	4	27	-	-
Mn	25	-	-	-	-	12	21
CoMn1	67	1.25	0.94	6	10	4	13
CoMn1.5	51	0.6	0.50	6	5	5	19
CoMn3	36	0.3	0.10	0.9	1.1	7	18

Fig. 1. XRD pattern of all studied samples

Fig. 2. XP spectra of studied samples: A) $Co2p_{1/2}$ region; B) Mn2p region.

TPR profiles of all samples are shown in Figure 3. The monometallic Co sample exhibits two reduction peaks at around 314 °C and 382 °C. These two peaks fit well in the reduction interval of bulk Co_3O_4 powder or supported relatively large Co_3O_4 particles [24]. The peak at 314 °C is attributed to the reduction of Co_3O_4 into CoO and that at 382 °C originates from the further reduction of CoO into Co^0. Hydrogen consumption at 302 and 433 °C is registered with the single-component manganese sample. These two reduction peaks are ascribed to the subsequent reduction of Mn_2O_3 into Mn_3O_4 and further into MnO [25].

Several overlapping peaks are appeared in the region 220-420 °C of bi-component samples. As is visible from TPR data of mono-component samples, cobalt and manganese oxide are reduced within the same temperature interval and it is difficult to make a correct assignment of the reduction peaks to the respective oxide phases. According to the authors of ref. [26] and [27] hydrogen consumption at 280 and 360 °C is due to the reduction of highly dispersed manganese oxide phase, probably in the form of 2D epitaxial layers. As it is seen from XRD (Fig. 1) the reflection patterns for Co-Mn catalyst are very broad and low intensive indicating finely dispersed particles. The low reduction temperatures for bi-component samples are with accordance with particle size effect — the smaller the particle size, the lower is the registered reduction temperature. We suggest that the reduction peaks in the temperature interval 220-420 °C come from the reduction of finely divided MnO_x and Co_3O_4 particles. The appearance of a broad peak of hydrogen consumption above 450 °C for Co-Mn oxide
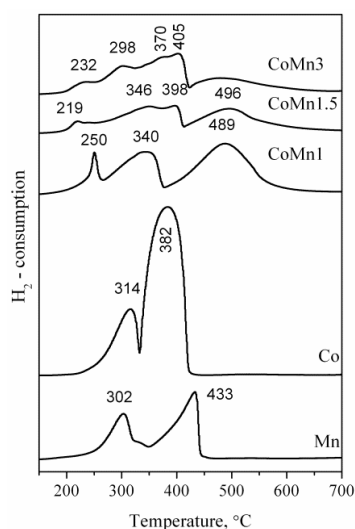
catalysts prepared by co-precipitation was already mentioned in [20]. It could be associated with reduction of a Co-Mn mixed oxide. Das *et al.* [28] reported the reduction of pure $(Co_{1-x}Mn_x)_3O_4$ phase at a temperature slightly above 600 °C. Due to the presence of many different phases, which are being reduced within the same temperature interval, the quantitative analysis of the TPR profiles of bi-component catalysts cannot be accurate.

The temperature dependences of the complete *n*-hexane oxidation over the mono- and bi-component catalysts are shown in Figure 4. H_2O and CO_2 were the only detectable reaction products of *n*-hexane oxidation on all investigated samples. The order of activities is as follow: CoMn1>Co> CoMn3>Mn> CoMn1.5.

It is well known that oxide catalysts operate in the oxidation reactions through a Mars -van Krevelen mechanism [14, 20]. According to this mechanism the VOCs are oxidized by the solid. The oxygen species introduced in the organic molecule come from the lattice. In this way the catalytic behaviour can be correlated to the lattice oxygen mobility. The lattice oxygen mobility is associated with the catalyst reducibility [29]. According to the TPR data, the reduction behavior of all bi-component samples is similar. Therefore in order to explain the difference in the catalytic activity it is necessary to search for another reason. One possible explanation is a very low crystallinity of the cobalt and manganese oxides, as it is visible from XRD data and as a consequence an increase in the concentration of the accessible active sites in these samples. The additional factor could be the simultaneous presence of Mn^{4+}–Mn^{3+} couple.

Fig. 3. TPR profiles of single- (Co, Mn) and bi-component (Co-Mn) oxides.
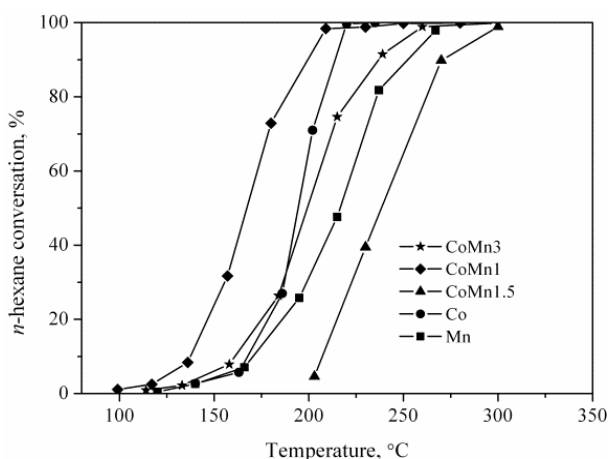
Fig. 4. Catalytic activity testing of investigated materials

It was established that catalytic activity increases when the pair Mn^{4+}-Mn^{3+} exists in the structure of the manganese oxide [20]. The other reasons for a considerable improvement in activity of CoMn1 sample could be the highest specific surface area and the simultaneous presence of Co^{2+} and Co^{3+} ions on the surface. It is well accepted that Co^{3+} is the catalytic active species in the oxidation reactions, but the presence of Co^{2+} can additionally impact on the activity, because Co^{2+} located at a relatively opened coordination position can be a centre for oxygen adsorption and formation of active oxygen species, which are a prerequisite for catalytic oxidation [6]. Obviously there are optimal ratios of Co^{2+}/Co^{3+} and Mn^{3+}/Mn^{4+} in the bi-component catalysts, which control the catalytic activity. Although the sample CoMn3 has a lowest surface area in comparison with the other bi-component oxides and manganese is the predominant component of the surface (see XPS data), it demonstrates relatively high catalytic activity. One possible explanation is the phase composition. From XRD data (Fig. 1) ilmenite $CoMnO_3$ structure was identified in this sample. It has been shown that the ilmenite-type catalysts were significantly more active for the complete catalytic oxidation of hydrocarbons [30].

CONCLUSION

The co- precipitation method used for the synthesis of bulk Co-Mn mixed oxide is suitable for obtaining catalysts with good catalytic performance in *n*-hexane oxidation reaction. All studied bi-component samples consisted of finely dispersed and easily reducible oxides. A significant improvement of the activity was observed over CoMn1 catalysts with a Co/Mn molar ratio of 1:1. The doping of manganese into the spinel structure of cobalt oxide decreases the crystallinity of the cobalt oxide thus increasing crystal defects, which probably causes an increase of the amount of divalent cobalt cations in a relatively opened coordination position. The coexisting of pairs Co^{2+}-Co^{3+} and Mn^{3+}-Mn^{4+} with the predominance of Co^{3+} and Mn^{4+} species and the highest specific surface area are responsible for the highest catalytic activity of the CoMn1 sample.

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Co-Mn СМЕСЕНИ ОКСИДНИ КАТАЛИЗАТОРИ ЗА ПРЕЧИСТВАНЕ НА ОТПАДЪЧНИ ГАЗОВЕ ОТ *n*-ХЕКСАН

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(Резюме)

Чрез методът на съутаяване са получени едно- и двукомпонентни Co-Mn оксиди. Те са изследвани с различни физикохимични методи (XRD, TPR and XPS) и изпитани в реакцията на пълно окисление на *n*-хексан. Най-високата каталитична активност проявява катализатор с молно съотношение Co/Mn=1. Едновременното присъствие на двойките Co^{2+} - Co^{3+} и Mn^{3+} - Mn^{4+} с преобладаващи концентрации на Co^{3+} и Mn^{4+} йони, високата специфична повърхност, както и ниската степен на кристалност допринасят за най-висока каталитична активност на образец CoMn1.

Ключови думи: *пълно окисление на хексан, кобалт-манганови катализатори, рентгенов фазов анализ, рентгенова фотоелектронна спектроскопия.*