SYNTHESIS OF CORDIERITE - MnOx - BLOCK CARRIERS CO OXIDATION CATALYSTS

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Abstract: The synthesis conditions were studied and the physicochemical of block cordierite supports with a secondary Mn – coating for the preparation of CO oxidation catalysts were determined.

Keywords: CO oxidation; manganese oxides; Cordierite - MnOx carriers; phase composition; specific surface .

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INTRODUCTION

Block carriers are widely used for the preparation of automotive catalysts [1]. To achieve the required porous structure, secondary coatings are applied on their surfaces in the form of heat-resistant oxides (CaO, MgO. Al_2O_3). All known block catalysts contain platinum group metals. However, these catalysts are expensive and mechanically insufficiently strong due to the difficulty of achieving the necessary adhesion of the secondary carrier to the frame material. The use of oxides of cobalt, copper and manganese [2,3] is promising for the preparation of automotive catalysts. Catalysts based on cobalt oxides make it possible to reduce the temperatures at which the maximum oxidation states of CO [4] and methane [5] are reached. Compared with cobalt and copper oxides, manganese oxides are thermally more stable.

Manganese stable oxides MnO_2, Mn_2O_3, Mn_3O_4 and MnO are differ from one another by their cristallochemical as well as by adsorbtion and other physical-chemical properties. Electron structure of mentioned oxides significantly varies (depending on the oxygen content) which, probanly, has a pronounced effect on their catalytic activity. The certain correlation between the value of the potential of surface and activity of manganese catalyst was established in the reaction of CO – oxidation depending on the process temperature[6] .

In a number of processes occurring in a reducing environment (oxidation of CO synthesis gas, hydrogenation of organic sulfur compounds and nitrogen oxides with hydrogen), favorable kinetic and thermodynamic conditions are created on a manganese catalyst, the composition of which is closer to Mn_3O_4 [7.8]. With oxygen deficiency, a decrease in the proportion of the MnO_2 phase at the metal-oxide - MnO_2 / Pt interface was recorded, with a simultaneous increase by orders of magnitude in the rate of the CO oxidation reaction. Based on the observed trend, Mn_3O_4 was identified as the dominant phase for increasing the rate of the CO oxidation reaction at the metal-carrier interface[9] . In accordance with Ref. [10, 11] , the particles of palladium are dispersed in the matrix of MnO_2. The addiction of palladium to the oxide - manganese catalist leads to the formation of new centers at the oxide / metall – MnOx / Pd interfaces phases which are active in the reaction of CO oxidation. These properties make manganese oxides the main active component of the secondary coating in block - cordierite CO oxidation catalysts. The results of studying the synthesis conditions and determining the basic physicochemical properties of block cordierite - carriers with Mn - coating for the preparation of CO oxidation catalysts are presented.

EXPERIMENTAL PART

The manganese oxides used were deposite on plates and ground particles (Ø 1,5 – 2,0 mm) of cordierite - $(Mg, Fe)_2 Al_{14}.Si_5.O_{18}$, blocks via impregnation with aqueous solution of manganese (II) nitrate. The samples prepared in this way were dried at 80-100 °C then calcined at 400 °C and 800 °C for 2 h. For laboratory tests on prepared - Cordierite - MnOx carriers were deposited oxides of manganese and palladium [12] . X – Ray phase of carriers and catalysts was carried out at the device ДРОН -1 in monochromated copper Kα radiation. Thermal analysis was performed on a STA – 2500 device. ISM 65 LV scanning electron microspore was used to study the morfology of the catalyst surface. Specific surfaces of the samples were determined by application of the automated system ASAP 2020. In nitrate solutions, the contents of Mn^{2+}, Mg^{2+} and Fe^{3+} - ions were determined on an AAnalisys 200 atomic absorption spectrometer. Activity of the catalyst samples in the CO oxidation reaction was determined in a flowing plant at laboratory scale (G_{cat} = 1,0 g, composition of reaction mixture: 1, 0 vol. % of CO + air, volume rate of the gas W= 15 . 10^3 h^{-1}). Analysis of reagent mixture on CO content before and after reactor was carried out at the chromatograph

GeC – 2014 ("Shimadzu" mark) with Conductivity Detector.

RESULTS AND DISCUSSION

SEM pictures of the components of the cordierite on the cordierite – MnOx $^{400\,oC}$ and cordierite – MnOx $^{800\,oC}$ carriers at 1 μm of the showed of the oxides of Mn are distributed uniformly on the surface. Heat treatment at 800 ^{oC} results in coarsening of manganese oxide particles from 10–100 nm to 500–600 nm. The average concentration of Mg atoms in the cordierite support is 2-4 mass. %, in carriers cordierite – MnOx - 0.1 - 0.2 mass. %. With diffusion saturation of carrier fragments, the content of Mg^{2+} ions in the test solution reaches 25 - 30 g. dm^{-3}. The presence of Fe^{3+} iron ions was not shown by spectral analyzes. X- Ray phase analyses of the showed the presence of cordierite – MnOx $^{400\,oC}$ phases β - MnO_2 (base) and α - Mn_2O_3 (traces). Additional high-temperature heat treatment at 800 ^{oC} leads to the completion of the process of formation of the crystalline structure of the secondary Mn - block carrier coating. In the cordierite – MnOx $^{800\,oC}$ sample, only the - α -Mn_2O_3 phase was identified (Fig. 1, b). The introduction of Mn atoms in the framework structure of the carrier provides the required adhesion of the secondary Mn coating on the surface of the block catalyst.

The characteristic propertis of the cordierite on the cordierite - MnOx $^{400\,oC}$ and cordierite - MnOx $^{800\,oC}$ are showed in Table 1. The successive application of a secondary coating of MnOx oxides increases the specific surface area of the cordierite block to 5.0 - 6.0 m^2. g^{-1}. The content of MnOx, in terms of Mn - metallic, reaches 5.5 - 6.0 wt. % (Table 2).

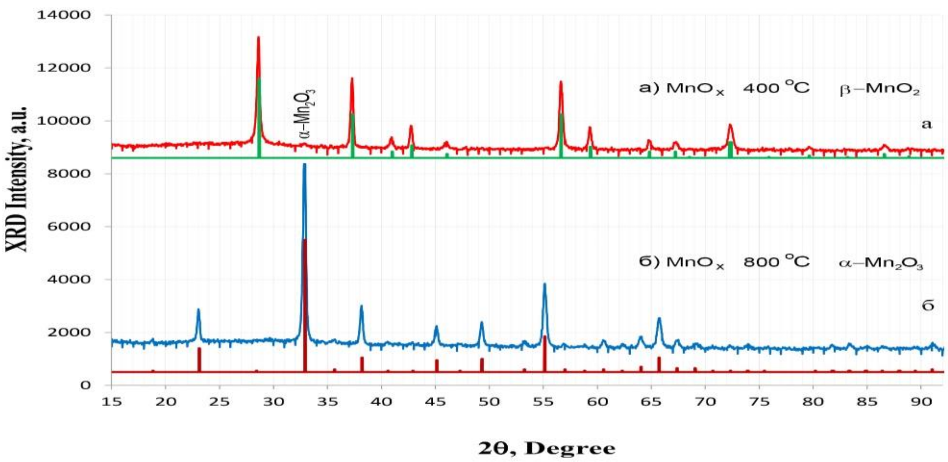

Figure 1. Diffractograms of the Al.Si - MnOx 400 oC (a) and Al.Si - MnOx 800 oC (b) catalists.

Table 1. The characteristic properties of the cordierite cordierite - MnOx400 oC and cordierite – MnOx800 oC carriers obtained from the N2 phisisorption measurements.

Sample name	BET Surface Areas, m^2/g	Micro Pore, m^2/g	Average Pore, m^2/g
Cordierite	0,669	0,4771	0,1919
Cordierite - 800 ºC	0.1082	0, 3159	-0, 2077
Cordierite - MnOx $^{400\,oC}$	1,2536	0,7685	0,5194
Cordierite -2 MnOx $^{400\,oC}$	3,2986	0,1277	3,1709
Cordierite- 3 MnOx $^{400\,oC}$	5,9245	0,1588	5,7657
Cordierite - MnOx $^{800\,oC}$	0,735	0, 2406	0,5020
Cordierite - MnOx $^{800\,oC}$/ MnOx $^{400\,oC}$	2,6136	0,7555	2,8561
Cordierite- MnOx $^{800\,oC}$/ 2 MnOx $^{400\,oC}$	5,2123	0,1425	5,0698

Table 2. Physical-chemical characteristics of cordierite - MnOx400 oC and cordierite – MnOx800 oC carriers.

Sample name	Content of Mn, mass.%	Phase composition
Cordierite - MnOx $^{400\,oC}$	1,8 – 2,0	β - MnO_2
Cordierite -2 MnOx $^{400\,oC}$	2,8 – 3,5	β - MnO_2
Cordierite- 3 MnOx $^{400\,oC}$	4,5 – 6,0	β - MnO_2
Cordierite - MnOx $^{800\,oC}$	1,7 – 2,1	α - Mn_2O_3,
Cordierite - MnOx $^{800\,oC}$ / MnOx $^{400\,oC}$	3,0 – 3,5	α -Mn_2O_3 , β - MnO_2
Cordierite- MnOx $^{800\,oC}$ / 2 MnOx $^{400\,oC}$	5,5 – 6,0	α -Mn_2O_3 , β - MnO_2

Physical-chemical characteristics and activity of the Pd - MnOx - catalyst, deposited on cordierite carrier, was studied in the CO oxidation reaction . A positive effect on the activity of the Pd - MnOx / Cordierite catalyst was shown to be treated with aqueous ammonia. Exoeffects on the DTA thermal analysis wing with maxima at temperatures of 255 ºC and 305 ºC were attributed to the phase dissociation of the formed amine-palladium complex. In all likelihood, palladium diamine chloride [Pd (NH_3) Cl $_2$] , which decomposes to form palladium black[12]. X-Ray phase and thermal analyses of the catalyst showed the presence of PdO and PdO_2 (traces). The endoeffect on the ДТА curve at the temperatures 780 ºC и 826 ºC wich in indicative of the phase decomposition of PdO.

Table 3. CO conversion of the Mn – Pd Catalists

Sample name	20 % CO Conversion	50 % CO Conversion	80 - 100% CO Conversion
Cordierite - MnOx $^{400\ oC}$ / Pd [12]	145 ºC	160 ºC	170-185 ºC
Cordierite - MnOx $^{800\ oC}$ / Pd	150 ºC	165 ºC	175-190 ºC

On catalysts Pd - MnOx 400 ºC / cordierite and Pd - MnOx $^{800\ oC}$ / cordierite, the maximum conversion of CO - 80 - 100% is achieved in the temperature range 170 - 190 ºC (Table 3). Modifications β - MnO_2 and α - Mn_2O_3 in Mn-Pd catalysts can be considered as active intermediate phases at the carrier-Pd interface.

CONCLUSIONS

The formation of a secondary Mn-coating at the interface Cordierite - Pd improves the physico-chemical characteristics and positively affects the activity of Mn - Pd CO oxidation catalysts.

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2. The contribution of the authors V.Bakhtadze and V.Mosidze consists in obtaining and processing experimental and published data.

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