

SiC nanofibers in canals and pores of cordierite honeycomb material as a support for catalyst in CO-PROX reaction

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The Cu–Co oxide system supported on SiC nanofibers deposited on cordierite was studied in the CO oxidation reaction in the presence of hydrogen.

Introduction

High efficiency and ecological safety, which are characteristic for the fuel elements (FE), activate the search of ideal fuel and a way of its refining, because the FE could be an alternative energy source for humanity. One of the fuels for the FE is hydrogen. It is produced by the vapor conversation, partial oxidation or autothermal reforming of hydrocarbons with further water-gas shift reaction. But such hydrogen-containing gas mixtures contain about 1 % of CO that decreases the efficiency of the fuel element because of its adsorption on the highly porous platinum anode of the FE. Hence, gas mixtures should be purified from CO admixture. Selective catalytic oxidation of carbon monoxide is one of the simplest and the most effective methods of the gas mixtures purification from CO admixtures.

Over the last few decades honeycomb monoliths made of cordierite with automobile

exhaust catalyst deposited on them showed good activity in selective CO oxidation. But they have such lacks as insufficient stability, low specific surface area and short lifetime. One of the effective methods to eliminate these defects is the deposition of SiC nanofibers, which have high thermal stability and oxidation resistance, on the surface of cordierite canals.

Results and discussion

In this study two types of support were selected: silicon carbide nanofibers (NF) and the same nanofibers fixed on cordierite (NF + C).

Catalysts were prepared by impregnation of a support by aqueous solutions of different metal nitrates with further evaporation and drying at 120 °C for 8 h and forming in the reaction mixture (75 vol.% H₂, 1 vol.% CO, 2 vol.% O₂, 22 vol.% He) within 2 h. It should be noted that

the active mass was the oxide system with the following composition: 85 wt.% Co, 15 wt.% Cu.

Quantity of the active mass deposited on a support was 10, 15 and 20 % of the initial support mass. It should be mentioned that deposition of the active mass in the quantity more than 20 wt.% causes allocation of the Cu-Co oxide system separately from the support, which is not desirable for quality assessment of support properties.

Fig. 1 shows the temperature dependences of the conversion of CO to CO₂ and selectivity towards CO oxidation over the sample with 20 wt.% of the active mass deposited on NF. From the figure it is obvious that 100% CO conversion (t^{100}) over this sample is reached at 190 °C.

For the sample with 15 wt.% of the active mass deposited on NF+C the temperature "counterclockwise" hysteresis is observed on the CO conversion curve, which can be explained by the presence of the fragments that contain hydrogen on the surface. The presence of hydrogen-containing particles promotes the transition of the reaction in the surface layers of the catalysts and, respectively, realizes the additional homogeneous mechanism that at the low temperature gives higher values in the CO conversion. Hysteresis is also available for some of the other samples.

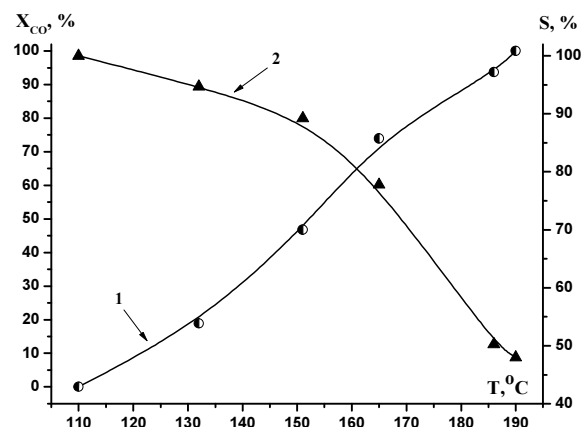


Fig. 1. The temperature dependences of the conversion of CO to CO₂ (1) and selectivity towards CO oxidation (2) over the sample with 20 wt.% of the active mass deposited on NF.

Table 1 shows the temperature of 100% conversion of CO to CO₂ and selectivity towards CO oxidation at t^{100} for the catalysts studied. The most active catalysts are the samples with 15 wt.% and 20 wt.% of the active mass deposited on bulk nanofibers, and the least active – the sample with 20 wt.% of the active mass deposited on cordierite. The selectivity of all catalysts is rather low.

In order to clarify the influence of the presence of nanofibers on the catalytic activity, the sample 6 was synthesized by deposition of corresponding metal nitrates on cordierite without SiC nanofibers ($t^{100} = 265$ °C, $S = 50$ %). This sample appeared to be less active than the sample 9 with the same amount of the active mass deposited on nanofibers, which were fixed on cordierite ($t^{100} = 219$ °C, $S = 54$ %).

Table 1. The temperatures of 100% conversion of CO to CO₂ and selectivity towards CO oxidation for the Co-Cu oxide catalysts studied

No	Support and amount of the active mass, wt. %	Amount of the active mass, 10 ⁻³ g and selectivity, (%)	<i>t</i> ¹⁰⁰ , °C
1	NF (0)	0	300, no conversion
2	NF (10)	36,8 (52)	198
3	NF (15)	55,2 (43)	190
4	NF (20)	73,6 (48)	190
5	C (0)	0	300, no conversion
6	C (20)	6,32 (50)	265
7	NF + C (0)	0	300, no conversion
8	NF + C (15)	4,74 (35)	240
9	NF + C (20)	6,32 (54)	219

After the catalytic experiment all samples were transferred to a quartz cuvette and then were evacuated with further recording of TPD-MS profiles.

TPD-MS profiles for the samples with 15 wt.% and 20 wt.% of the active mass deposited on SiC nanofibers taken before the reaction are presented in Fig. 2.

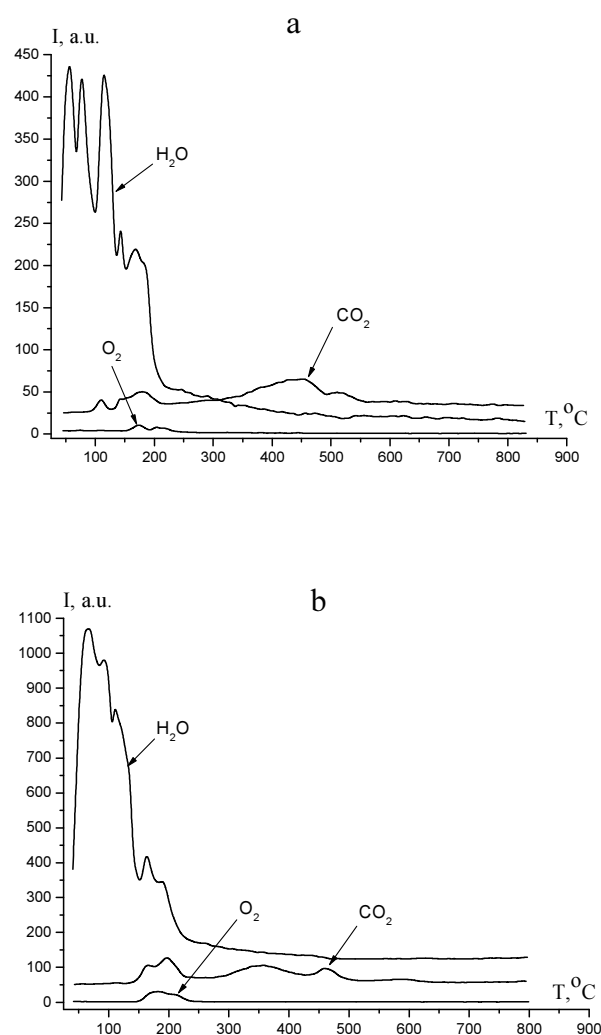


Fig. 2. TPD-MS profiles of H₂O, CO₂ and O₂ for the samples with 15 wt.% (a) and 20 wt.% (b) of the active mass deposited on SiC nanofibers taken before the reaction.

For both samples low-intensity peaks of oxygen are observed at about 200 °C.

Water is desorbed from the surface in large quantities in the temperature range from 50 to 220 °C (so called weakly bounded form of water). The peaks are described by symmetrical forms, which indicates about the recombination desorption, thus from catalyst surface OH⁻ groups desorb in the surface layer

with further recombination into the molecule of H₂O.

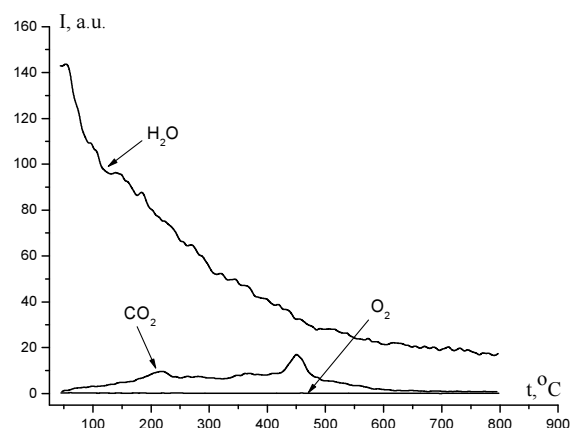
CO₂ is desorbed from the catalyst surface in the following forms, which are distinguished by temperatures of TPD-MS maxima peaks: α₂ (t_m = 100-200 °C), α₄ (t_m > 300 °C). Asymmetrical forms of peaks indicate molecular desorption of CO₂ from the catalyst surface.

At temperature of 180 °C desorption peaks of oxygen, water and carbon dioxide are observed simultaneously. This could indicate a high activity of the samples in the CO-PROX reaction [3].

Fig. 3 shows TPD-MS profiles for the samples with 10 wt.% and 15 wt.% of the active mass deposited on SiC nanofibers taken after the reaction.

According to the obtained data it is clearly seen that desorption of oxygen from the surface of the samples with 10 wt.% and 20 wt.% of the active mass is absent. Low-intensity peak of O₂ is observed at 630 °C for the sample with 15 wt.% of the active mass.

a



b

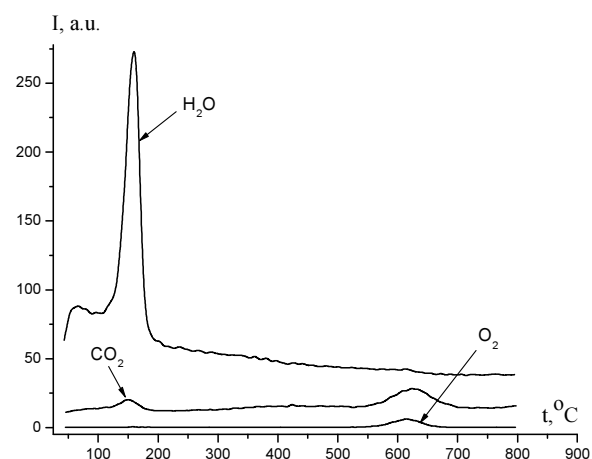


Fig. 3. TPD-MS profiles of H₂O, CO₂ and O₂ for the samples with 10 wt.% (a) and 15 wt.% (b) of the active mass deposited on SiC nanofibers taken after the reaction.

For the sample with 10 wt.% and 20 wt.% of the active mass (sample 2 and 4) desorption of water is observed up to 500 °C. From surface of the sample with 15 wt.% of the active mass (sample 3) water is desorbed up to 200 °C.

CO₂ is desorbed in the following forms: α_2 ($t_m = 100 - 200$ °C), α_3 ($t_m = 200 - 300$ °C) and α_4 ($t_m = 300$ °C and above). The peaks are asymmetric, what indicates the nature of the molecular desorption.

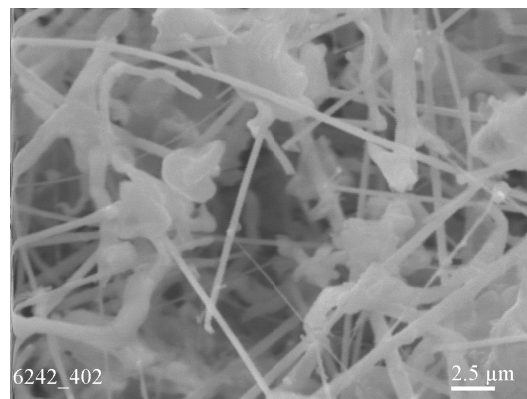
The feature of the samples 3 and 4 is the presence of peaks of H₂O and CO₂ at the same temperature (160-170 °C). As it was mentioned above, these samples are characterized by lower t^{100} than sample 2. Thus, there is a correlation between the presence of α_2 form of CO₂ desorption and catalytic activity.

The distribution of particles on the surface can be seen from SEM-photographs of the sample with 20 wt.% of the active mass deposited on NF (Fig. 4). According to the SEM-photographs NF are in linear and curved shapes. The length of the NF is up to 0.19 mm and the diameter is in a range from 0.17 to 2.85 μm . The active phase locates on the surface of the NF in finely dispersed state and as separate aggregates, which are placed on the NF and in the intervals between them, and are not changed after the CO oxidation.

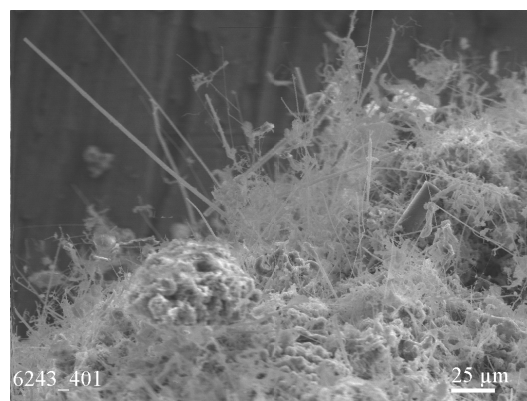
Thus, the catalysts obtained by the deposition of the Cu-Co oxide system on bulk SiC nanofibers appeared to be more active than on SiC nanofibers fixed on cordierite, which can be explained by the big difference in active mass deposited (Table 1).

Thus, this investigations show that Cu-Co oxide system supported on SiC nanofibers

deposited on honeycomb cordierite exhibit high catalytic activity and selectivity in CO-PROX reaction and represents a scientific interest.



a



b

Fig. 4. SEM-photographs of SiC nanofibers with 20 wt.% of the active mass (a – before the reaction; b – after the reaction).

Conclusions

The physicochemical characteristics of the Cu-Co oxide system deposited on bulk SiC nanofibers and on SiC nanofibers, which were fixed on cordierite, were studied; and the catalytic activity in the reaction of the selective CO oxidation was examined.

It was found that on the surface of the deposited oxide Cu-Co catalysts carbon monoxide adsorbed in several forms. According to the TPD-MS profiles α_2 form of CO₂ desorption is available on the surface of the most active samples ($t_m = 100 - 200$ °C) and is responsible for the low temperature oxidation of carbon monoxide.

It is shown that SiC nanofibers, which were fixed on cordierite, promote more uniform distribution of the active mass in the volume of the support and increase catalytic activity in the CO-PROX reaction.

Experimental part

In this study catalyst supports were synthesized by chemical vapor deposition, using a CH₃SiCl₃+H₂ mixture in the presence of Fe in a flow-type quartz reactor mounted in a horizontal tube furnace. The temperature was 1250-1350 °C, the time of reaction – 5-10 min. The cordierite honeycomb (Al₂O₃)₂(SiO₂)₅(MgO)₂, synthesized in Frantsevich Institute of Materials Science Problems (Kyiv) was used as an underlay. The size of canals is 1,0 mm x 1,0 mm and the thickness of walls is 0,18 mm [1]. The Cu-Co oxide system (15 wt. % Cu, 85 wt. % Co) was used as an active mass [2].

The catalytic experiment was carried out in a flow reactor at atmospheric pressure with a chromatographic analysis of the reaction mixture using a SHIMADZU

GC-2014 chromatograph, molecular sieve 5A column. Temperature of 100% CO conversion (t^{100}) was used as a measure of catalytic activity. The morphology of SiC nanofibers with formed active mass was studied using scanning electron microscopy (SEM).

Species adsorbed on the surface of the samples were studied by thermally programmed desorption (TPD) with mass spectral (MS) analysis of desorbed particles. After the reaction, the samples were immediately transferred into the quartz reactor connected to mass spectrometer chamber. TPD-MS spectra were recorded using an MX7304A mass spectrometer with linear heating of the samples at the rate of 14 K/min.

References

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- [3] Ockwig N. W., Nenoff T. M. *Membranes for Hydrogen Separation // Chem. Rev. – 2007. – V. 107. – P. 4078-4110.*