Influence of the carrier phase composition on the catalytic activity of copper-cobalt oxides deposited on slag glass-ceramics

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In order to check to what extent the slag based glass-ceramics may be used as carriers in the preparation of active supported catalysts, copper-cobalt oxide catalysts on different carriers (glass-ceramics obtained on the basis of blast furnace slag) were studied. The catalytic activity towards the complete oxidation of carbon monoxide was evaluated. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET analyses. Three main crystalline phases were present in varying proportions in the catalyst carriers: melilite, anorthite and pyroxene. The results of catalytic tests were interpreted with respect to the catalyst carrier phase composition. It was found that the catalytic activity and the formation of catalytically active complexes depend on the phase composition of the carrier. Among the crystalline phases present in the composition of the carriers, pyroxene contributes to the formation of the most efficient catalytically active complexes.

Keywords: Phase composition, supported catalysts, catalytic activity.

INTRODUCTION

Regardless of its variable composition, blast furnace slag can be successfully used as an adsorbent or as a carrier for the preparation of catalysts for full oxidation. It has been found that this is possible because of the presence of crystalline phases of the melilite group. They determine the adsorption capacity of the slag to the ions of some heavy metals such as lead, copper and the like [1–8], whereas the inclusion of transition metal ions in the crystalline structure yields catalysts for the oxidation of CO and hydrocarbons [9, 10].

The preparation of catalysts, the active phase of which is deposited on a carrier, requires the synthesis to be conducted so that there are catalytically active complexes (CAC) on the surface of the carrier [11–14]. It is essential that the carrier and its chemical nature play an important role in CAC when there are deposited catalysts, since a variety of ions from the deposited phase, but also from the carrier may be involved in it [11–14]. Therefore, the same catalytically active phase deposited on different carriers has different catalytic activity in the same catalytic reaction. It is of interest to check to what extent the slag glass-ceramics obtained on the basis of blast furnace slag, may be used as carriers for the preparation of catalysts by depositing oxides of 3d-transition

metals. For slag glass-ceramics of this type, it has been shown that the crystal structure of the phases in them conditions the adsorption capacity to the ions of lead [15].

Therefore, the aim of this paper was to study the influence of phase composition of slag glass-ceramics which were used as a carrier of copper-cobalt oxides in reactions of CO oxidation.

EXPERIMENTAL

Synthesis of the carriers

To obtain the carriers – slag glass-ceramics, kaolin, Al_2O_3, and TiO_2 were used, as well as granulated blast furnace slag with the following composition – CaO (40.5%), SiO_2 (35.2%), A_2O_3 (9.3%), MgO (5.2%), BaO (3.2%), MnO (2.6%), S (1.2%), K_2O (1.0%), Na_2O (0.3%), FeO (1.0), Fe (0.7%). First, the parent glasses were prepared by melting at 1450-1470 °C for 60-90 min. Then the glasses were ground, pressed and heated at 1000 °C for 3 h. The method of synthesis of the samples is described in more detail in [16]. The choice of particular compositions and additives was based on our previous experimental data [17–19], which showed that high-strength glass-ceramics could be obtained from such compositions. Four sample carriers were obtained by changing the ratio of components with a view to the formation of different crystal phases. The carriers were designated as SC (a) with initial composition: 73.6% slag and kaolin 20.7%; SC (b) with initial

composition: slag 68.2%, kaolin 20.5%, Al_2O_3 5.7%; SC (c) with initial composition: slag 74.3% kaolin 12.0%, Al_2O_3 8.0% and SC (d) with initial composition: slag 79.9%, kaolin 12.2%, Al_2O_3 2.2%. In all batches, 5.7% of TiO_2 was added.

Synthesis of the catalysts

The obtained carriers were impregnated with a solution containing copper nitrate and cobalt nitrate with different concentrations, while maintaining the atomic ratio of Cu: Co = 1: 2. The procedure was carried out using a solution/carrier ratio of 5 (v/w) at a temperature of 90 °C for 1 h. Then the samples were left in the solution without heating for 24 h and the impregnation procedure was repeated once more. After impregnation and drying at 110 °C, the samples were heated in air at 350 °C for 3 h. The samples were labeled CAT (a), CAT (b), CAT (c) and CAT (d) and they were obtained from the respective carriers – SC (a), SC (b), SC (c) and SC (d).

Experimental methods

X-ray powder diffraction (XRD) analysis was applied for phase identification. An X-ray diffractometer Philips with Cu Kα radiation (λ = 1.5418 Å) was used in the range from 15° to 90° 2θ (step size: 0.05°, counting time per step: 1 s). The crystalline phases were identified using the powder diffraction file cards № 35-0755, 41-1486 and 31-0249 from database JCPDS - International Centre for Diffraction Data PCPDFWIN v.2.2. (2001)) [20].

The microstructure of the glass ceramic materials was investigated by SEM. Microscope JEOL JSM 5510 was used. The samples were coated with gold in an auto fine coater JEOL JFC-12200.

The concentration of the solutions used just after the procedure for the deposition of copper and cobalt phases was determined by ICP-OES analysis using Prodigy high-dispersion ICP-OES spectrometer from Teledyne Leeman Labs.

The measurement of the specific surface area of the samples was carried out by nitrogen adsorption at 77.4 K. Nitrogen adsorption isotherms were used to calculate the specific surface area using the BET equation.

The catalytic activity of the samples was measured in an isothermal plug-flow reactor enabling operation under steady-state conditions without any temperature gradients. The size of the catalyst particles (0.3 – 0.6 mm) was chosen taking into account the reactor diameter (6 mm) and the hourly space velocity (20 000 h^{-1}). The gas feed

flow rate was 4.0 L/h, the catalyst bed volume was 0.2 cm^3, and the mass of the charged catalyst was 0.50 – 0.55 g. The catalytic oxidation was performed within the temperature interval 200 – 400 °C, the oxidizing agent used being oxygen from the air (gas mixture: 21% O_2 and 79% N_2). The preliminary treatment of the catalysts included heating in air flow at 120 °C for 1 h. The flow of CO was fed into the reactor by an Ismatex M62/6 pump (Switzerland). The initial concentration of carbon monoxide was 0.5 vol. %. The carrier gas was air (a mixture of 21% O_2 and 79% N_2). A Maihak gas analyzer (O_2, CO, CO_2) was used to measure the CO and CO_2 concentrations with an accuracy of ±0.1 ppm, whereas the oxygen measurement accuracy was ±100 ppm.

RESULTS AND DISCUSSION

Table 1 presents the results of the identified crystalline phases, for the given specific surface and for the deposited amounts of copper and cobalt. As seen from the Table, three main crystalline phases in varying proportions are present in the samples: melilite, anorthite and pyroxene [15, 16].

The quantification of the contents of each of these phases in the samples showed the following: the phase content of sample CAT (a) was anorthite accounting for slightly more than 50% of the crystalline phases. The compositions of CAT (b) and CAT (c) were characterized by a more significant participation of pyroxene in the phase content; 40-51% of the crystalline phases and melilite was the predominant crystal phase only in sample CAT (d).

From the data in Table 1 for specific surface area, it is obvious that the samples differ in this indicator; the highest one is that of CAT (d). The samples also differ in contents of the two metals, but the atomic ratio is preserved and is approximately equal to two. As noted before, the preparation of the catalysts was conducted so that there were CAC with ratio Co / Cu = 2 on the surface, for which it is known to have high activity in oxidation reactions [21].

The microscopic images of the samples showed that they had very suitable microstructure for carriers of catalysts. Fig. 1 shows a microscopic image of the specimen CAT (d).

Common micro-structural features were observed in all slag glass-ceramics [15, 16]. There was a good sintering of the initial powders. The obtained glass-ceramic materials had a finely dispersed crystalline structure showing microcrystals of ~ 3-4 μm. Amorphous phase densely envelopes the crystals. Idiomorphic crystals

with a characteristic morphology that corresponds to anorthite, melilite and pyroxene, respectively, were identified in large rounded pores measuring up to 10-20 μm. The pores observed in our study (Fig. 1) were typical intragranular induced crystallization pores. We consider it probable that these pores were formed as a consequence of the crystallization of glass. The crystals formed in the amorphous matrix had a higher density than the density of the amorphous mass, which led to shrinking of the sample and the formation of induced porosity.
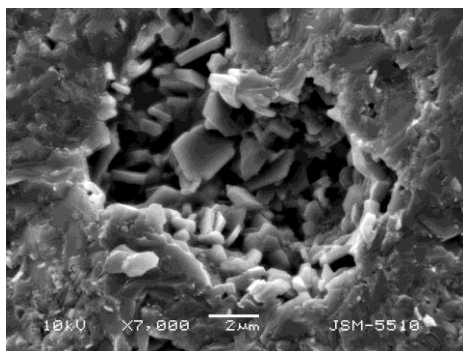

Fig. 1. SEM image of the sample CAT (d).

It was important to get information about the obtained crystalline structure containing copper and cobalt. Fig. 2 shows the X-ray-diffraction data for catalyst CAT (d), since according to chemical analysis, Table 1, this sample contains the highest amounts of the deposited phases and it is expected that this may have an impact on X-ray patterns.
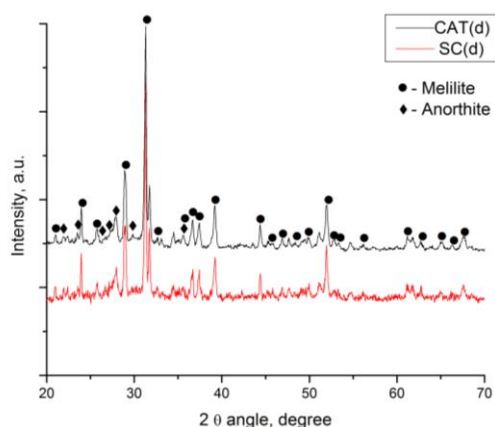

Fig. 2. X-ray diffraction data about catalyst CAT (d) and carrier SC (d)

For comparison, the X-ray pattern of the original sample used for obtaining the sample carrier SC (d) is shown. These diffraction patterns, as shown in Fig. 2, are almost identical, so unfortunately the newly formed copper- and cobalt-containing phases cannot be identified on the basis of XRD. The presence of the following crystalline phases is likely: CuO, Co_3O_4, $CuCo_2O_4$, but due to the small

quantities and the possibility of their most intense diffraction peaks to overlap with the peaks of the diffractogram of the carrier, they cannot be confirmed by XRD.

Figures 3 and 4 present the results of testing the catalytic activity of the catalysts. Fig. 3 shows data for the catalytic activity – η as a degree of CO oxidation in %. The catalytic activity given as an amount of oxidized CO per gram of catalyst – intensity (Ig) is presented in Fig. 4.
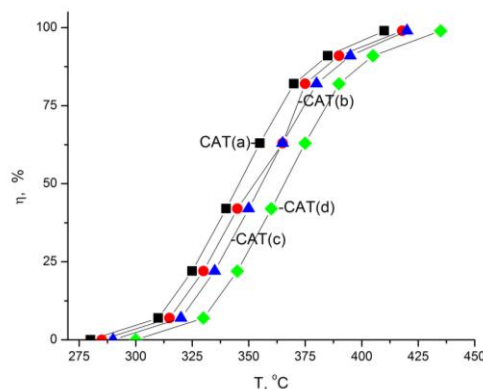

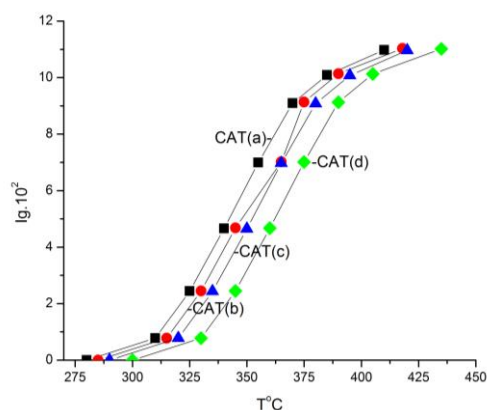**Fig. 3.** Degree of conversion of CO [η,%] in dependence on temperature [T, °C].

Fig. 4. Dependence of the amount of oxidized CO of 1 g catalyst for 1 hour [Ig] on temperature [T, °C]

As it can be seen from the figures, the most active catalyst regarding both indicators is the catalyst CAT (a), and the least active one is the catalyst CAT (d). The difference in the activity of the catalysts is not huge, as it can be seen from Table 2, where the values for η and Ig at temperatures 365 ° C are given. As the Table shows, the values for the parameter η are grouped in the range 76-49%. The same is true for the Ig. For CAT (a) Ig = $8.40 \cdot 10^{-2}$, whereas for CAT (d) Ig = $5.45 \cdot 10^{-2}$, despite the fact that the latter catalyst has the highest specific surface area (Table 1). This proves that this parameter – specific surface, is not decisive. The basic indicator must be the amount of the deposited oxide phases and their activity efficiency – namely, the activity of formed CAC. In

order to clarify how effectively the oxides of copper and cobalt are used, the intensity (Ig) for one gram of total content of copper and cobalt in the catalysts (Ig_{Cu+Co}) was estimated. The results of this calculation are shown in Figure 5.
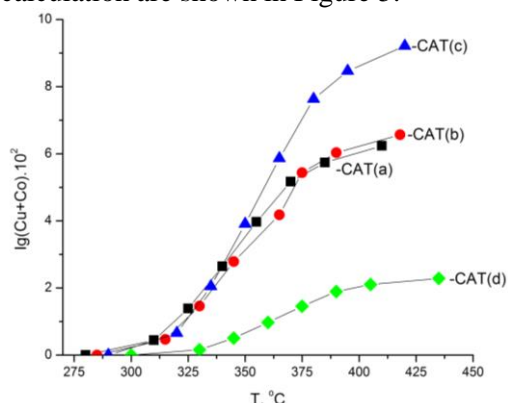
Fig. 5. Dependence of the amount of oxidized CO of 1 g (Cu + Co) for 1 hour $Ig_{(Cu+Co)}$ on temperature [T, °C]
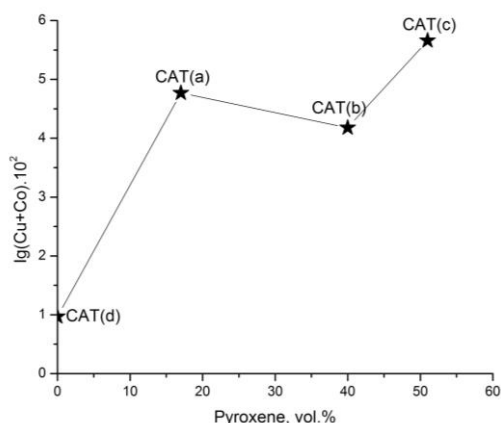
Fig. 6. Dependence of the intensity of the catalysts – $Ig_{(Cu+Co)}$ at 365 °C on the content of pyroxene.

It can be seen from the figure that the sample CAT (d) again has the lowest activity. In this case the differences in activity are significant. According to this indicator, CAT (c) exhibits the highest activity, although the contents of copper and cobalt in it are the lowest (Table 1). Accordingly, not only the amount of the applied oxides, but also the phase composition is important for the formation of CAC – the amount and type of crystallized phases. If you compare the data presented in Table 1 and Table 2 it is immediately clear that in the least active

catalyst CAT (d), the phase pyroxene is missing. If we assume that this phase promotes the formation of more active CAC, i.e., it plays a significant role, it would be logical that with the increase of its amount, the activity of the catalysts would also increase. Fig. 6 presents data about Ig_{CuCo} depending on the content of the crystalline phase pyroxene. Activity actually increases with the increase of pyroxene in the catalysts. Therefore, this crystalline phase results in the formation of the most active CAC. Of course, the role of anorthite should not be ignored, since the catalysts are active even in the absence of pyroxene. On the basis of the obtained results, it is possible to make a conclusion that anorthite contributes to the formation of more efficient CAC than melilite. These crystal phases belong to two main structural silicate types and the CAC formed differ. These data confirm that the carrier and its nature play an important role in CAC formation.

Table 2. Data for the catalytic activity at 365 °C.

Samples	η, %	$Ig.10^2$	$Ig_{CuCo}.10^2$
CAT(a)	75.7	8.40	4.77
CAT(b)	63.0	7.02	4.18
CAT(c)	63.0	6.97	5.66
CAT(d)	49.0	5.45	0.97

The activity of CAC depends on the generated Cu- and Co-containing phases; the formation of crystalline phases with spinel structure is desirable. The reason for the formation of more active CAC on carriers containing pyroxene is probably due to the ability of pyroxene to contribute to the heterogeneous nucleation of the spinel. An epitaxial relationship is widely observed in spinel exsolution lamellae within pyroxene [22, 23] facilitated by similar spacing and plane group symmetries of oxygen atoms of {010} pyroxene and {110} spinel. Hammer *et al.* [24], concluded that clustering and physical contact of pyroxene and spinel forming from melt develop from heterogeneous nucleation followed by epitaxial crystal growth. In the available literature we found no data on epitaxial relationships between spinel and anorthite or spinel and melilite.

Table 1. Phase compositions, BET surface area of the catalyst carriers and amount of copper and cobalt deposited

Sample	Crystalline phases, vol %			S_0, m^2/g	Content, weight %		Mol. ratio
	Melilite	Anorthite	Pyroxene		Cu	Co	Cu/Co
CAT(a)	32	51	17	17.7	0.62	1.14	1.90
CAT(b)	20	40	40	23.3	0.54	1.14	2.27
CAT(c)	26	23	51	31.2	0.40	0.79	2.13
CAT(d)	66	34	0	43.3	1.55	3.27	2.17

CONCLUSIONS

Based on the experimentally obtained results for the catalytic activity of copper and cobalt oxides deposited on slag glass-ceramics, it can be concluded that the formation of catalytically active complexes (CAC) depends on the phase composition of the carrier. Among the crystalline phases present in the composition of slag glass-ceramics, pyroxene contributes to the formation of the most efficient CAC whereas the influence of anorthite and melilite is weaker.

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ВЛИЯНИЕ НА ФАЗОВИЯ СЪСТАВ НА НОСИТЕЛЯ ВЪРХУ КАТАЛИТИЧНАТА АКТИВНОСТ НА МЕДНО-КОБАЛТОВИ ОКСИДИ НАНЕСЕНИ ВЪРХУ ШЛАКОСИТАЛИ

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(Резюме)

За да се провери доколко шлакоситали могат да се използват като носители за получаване на активни нанесени катализатори, са изследвани катализатори, получени чрез нанасяне на медно-кобалтови оксиди на различни шлакоситали. Каталитичната активност е изследвана по отношение окислението на въглероден оксид. Образците са охарактеризирани с помощта на рентгенодифракционен анализ, сканираща електронна микроскопия и BET-анализ. Установено е, че мелилит, пироксен и анортит в различни съотношения са основните кристални фази в тях. Резултатите от каталитичните тестове са интерпретирани във връзка с фазовия състав на носителите на катализаторите. Установено е, че каталитичната активност и формирането на каталитично активни комплекси зависят от фазовия състав на носителите. От кристалните фази в състава на носителите пироксенът допринася за образуване на най-ефективни каталитично активни комплекси.