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Catalytic oxidation of CO and hydrocarbons on SHS-prepared complex metal oxide catalysts

Yu.V. Tyurkin *[,1], E.N. Luzhkova, G.N. Pirogova, L.A. Chesalov

117915 Leninsky pr., 31, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia

Abstract

Complex metal oxides with the structure of spinel type $(Me^{II}_{A})(Me^{III}_{B})_2O_4$ based on Co, Ni, Cu, Mn, Cr, Al are synthesized by a self-propagating high-temperature synthesis method (SHS). IR spectroscopy and X-ray analysis are used for studying the structure of the oxides. The tests of the catalytic activity of the complex oxides in CO and hydrocarbons oxidation reactions have shown that the Co-Cr-Al complex oxides possess the most activity. Their activity depends on the ratio of Cr and Al in the spinels and increases with the increase of the chromium content. The samples synthesized in the SHS regime are more defective and, as consequence, more active than the samples produced by reaction sintering.

The SHS-catalysts have been manufactured as monolith cellular blocks and have been proven in an industrial application. Results of tests of these catalysts for purification of a waste gases are included.

Keywords: Catalyst; Catalytic oxidation; Complex oxide; Spinel; Carbon monoxide; Hydrocarbons; Self-propagating high-temperature synthesis; Cellular block

1. Introduction

One of the efficient methods of purification of the waste gases from CO and organic matter, type $C_nH_mO_x$, consists of their catalytic oxidation to nontoxic compounds, carbon dioxide and water. Used as catalysts are platinum group metals as well as oxides of copper, cobalt, nickel, manganese, etc. [1,2]. The maximum activity is demonstrated by the catalysts with platinum and palladium. However, their use is limited by a high cost. The oxide catalysts have less activity, but they are much cheaper than the catalysts with noble metals. Even though the operating temperature for the oxide catalysts is somewhat higher, it is within the limits permissible from the technical point of view. The main disadvantage of the oxide catalysts is their inadequate stability in the gaseous medium containing sulfur and hydrocarbons. Complex oxides of the spinel and perovskite type [3-5] demonstrate higher catalytic activity and stability as compared with individual oxides.

In conformity with the present publication, complex oxides were synthesized by the method of self-propagating high-temperature synthesis (SHS) which is at the present time widely used for synthesis of various compounds [6-8]. There were synthesized complex oxides with the structure of the spinel type $(Me^{II}_{A})(Me^{III}_{B})_2O_4$ based

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* Corresponding author.

[1] Present address: Benchmark Structural Ceramics Corp., 350 Nagel Drive, Buffalo, NY 14225, USA. E-mail: tyurkin@aol.com.

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on Co, Ni, Cu, Mn, Cr, Al. The catalytic properties of the SHS-spinels in the CO and hydrocarbon oxidation reactions were tested in the modelling and industrial conditions.

2. Experimental

2.1. Synthesis of complex oxides

The SHS method is based on exothermic interaction of the powderlike components in the mixture. The components and their ratio shall be selected so that the required compound is formed in the process of the synthesis and the heat produced in the reaction is sufficient for propagation of the zone of reaction in the combustion wave regime. For the synthesis of the complex oxides, we used oxides, hydroxides or carbonates of the respective metals and powderlike metallic Al in the capacity of the initial components. The synthesis was carried out in a special furnace allowing for initiation of the exothermic reaction both at room temperature and at a preheating temperature of up to 1000°C.

The scheme of the synthesis can be represented on the example system Co-Cr-Al-O as follows:

$$\begin{aligned}&1/3\mathrm{Co_3O_4} + x\mathrm{Cr_2O_3} + (1-x)\\ &\quad\times[2y\mathrm{Al} + (1-y)\mathrm{Al_2O_3}]\\ &\quad\rightarrow \mathrm{Co}[\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O_4} \qquad (1)\end{aligned}$$

The system is self-heated due to partial aluminum reduction of the cobalt oxide.

We have synthesized the following complex oxide systems: $\mathrm{Ni}[\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O}_4$, $\mathrm{Co}[\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O}_4$, $\mathrm{CuCrO_2}$-$\mathrm{CuCr_2O_4}$, $[\mathrm{Co}_x\mathrm{Cu}_{(1-x)}]\mathrm{Al_2O_4}$, $\mathrm{MnAl_2O_4}$, $\mathrm{Mn}[\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O}_4$, $[\mathrm{Co}_x\mathrm{Ni}_{(1-x)}]\mathrm{Al_2O_4}$, $[\mathrm{Co}_y\mathrm{Cu}_{(1-y)}][\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O}_4$, $\mathrm{Co}[\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O}_4$-$\mathrm{LaCoO_3}$, $[\mathrm{Mn}_y\mathrm{Cu}_{(1-y)}][\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O}_4$.

The main parameter characterizing the synthesis process is represented by combustion temperature T_c. Its value can be changed within wide limits by changing the composition of the initial mixture and preheating temperature. In this case, the phase composition and the structure of the synthesis products are substantially changed. The following main regularities which are characteristic of all above-mentioned systems can be established:

1. If the temperature in the process of the synthesis is high enough for production of a liquid phase in the system (commonly 1500–2000°C), the product is highly sintered, its specific surface area being below 0.1 $\mathrm{m^2/g}$. The composition of the complex oxide corresponds to the ratio of the components in the initial mixture.
2. If the liquid phase is not originated at T_c (commonly 950–1300°C), the composition of the complex oxide can differ from the rated composition, comprising unreacted initial oxides and intermediate products of interaction. The specific surface area of the synthesis products is 1–3 $\mathrm{m^2/g}$.

Preliminary tests of the catalytic activity of the synthesized complex oxides have shown that the samples in systems Co-Cr-Al-O and Cu-Cr-Al-O [9,10] are most promising. Therefore, the main attention in our further studies was given to these systems.

2.2. System Co-Cr-Al-O

It is known that with increase of the content of the chromium atoms in the structure of spinel $\mathrm{Co}[\mathrm{Cr}_x\mathrm{Al}_{(1-x)}]_2\mathrm{O}_4$, the lattice parameter a should change from 0.811 nm for cobalt aluminate to 0.833 nm for cobalt chromite [11] which makes it possible to approximately estimate the spinel composition by the data of the X-ray phase-shift analysis (XPA).

In the course of the SHS-synthesis of the complex oxides, we changed the ratio of the components in the initial mixture so as to synthesize the spinels differing in the content of Al and Cr from $\mathrm{CoAl_2O_4}$ to $\mathrm{CoCr_2O_4}$. In this case, the value of parameter x in Eq. (1) was changed from 0 to 1. The content of Al was selected for each value of x so that the synthesis was realized in the low-temperature regime (T_c = 1150–1200°C) and in the high-temperature regime (T_c is over 1700°C). It should be pointed out that at $x = 0.6$–0.8, the synthesis can be realized only in the low-temperature regime, and at $x = 1$ it can be realized in the reaction sintering regime [8].

The study of the synthesized samples by the XPA method has shown that when the synthesis is carried out in the high-temperature regime, the parameters of the lattice of the spinels produced at various values of x are close to the hypothetical values calculated on the assumption that the lattice parameter is linearly changed in transition from cobalt aluminate to cobalt chromite.

When making use of the low-temperature regime, the parameter of the lattice of the spinels being synthesized continuously increases with the increase of the chromium oxide content in the initial mixture but its values exceed the theoretical values for the respective initial compositions (Table 1). This testifies to the fact that the number of the chromium atoms in the spinel composition exceeds the number expected to be in the composition of the initial mixture. Already at $x = 0.7$–0.8, there is produced a spinel with $a = 0.832$–833 nm which corresponds to cobalt chromite.

Formation of the mixed spinels in the systems is proved by the data from infrared spectroscopy (Table 1). Spinels $CoAl_2O_4$ and $CoCr_2O_4$ are produced at $x = 0$ and $x = 1$, respectively. The position of the absorption bands in these spinels complies with the literature data [12]. When the content of Cr_2O_3 in the initial mixture increases (x changes from 0.2 to 0.8), the IR-spectra show that the absorption bands of the stretching vibrations (Me^{III}-O_o) and (Me^{II}-O_t) are consecutively shifted into a low-frequency region. The observed absorption bands are not characteristic either of cobalt aluminate or of cobalt chromite and belong to the spinels of the mixed composition $Co[Cr_xAl_{(1-x)}]_2O_4$.

Apart from the main spinel phase, the tested samples contained small quantities of unreacted initial oxides.

2.3. System Cu-Cr-Al-O

By changing the ratio of the components and synthesis conditions, it becomes possible to ob-

Table 1
The structural, combustion and CO conversion activity characteristics of SHS-prepared $Co[Cr_xAl_{(1-x)}]_2O_4$ complex oxides

Sample number	x [a]	Combustion temperature, T_c (°C)	Lattice parameter, a (nm)	Wavenumber Me^{II}-O_t ν_1 (cm^{-1})	Wavenumber Me^{III}-O_o ν_2 (cm^{-1})	Temperature of 100% CO conversion, $T_{100\%}$ (°C)
1	0	1200	0.811	669	561	210
2	0.2	1200	0.817	662	554	210
3	0.4	1200	0.821	649	533	200
4	0.6	1200	0.832	640	523	200
5	0.8	1200	0.833	622	514	180
6	0.8	1050	0.833	630	523 531 555	160
7 [b]	0.8	1000	0.833	622	514	220
8 [b]	1.0	1000	0.833	622	514	220

Specific surface area of all samples is about 1.5 m^2/g.

[a] x defines the molar correlation of Cr and Al in the initial mixture [x = Cr/(Cr + Al)].

[b] Synthesis was performed in the reaction sintering regime at T = 1000°C for 3 h.

tain in this system either univalent copper chromite $CuCrO_2$ mixed with Al_2O_4 or the mixture of $CuCrO_2$ and complex oxide, type $Cu[Cr_xAl_{(1-x)}]_2O_4$, having a tetragonal modification. It is not practicable to synthesize a complex oxide with the spinel structure which is explained by instability of the cubic modification of copper chromite at the temperature produced in the course of the synthesis (T_c is over 1000°C). However, the introduction of small additives of the cobalt oxide (up to 5%) into the initial mixture provides for production of a complex oxide with the structure of the spinel, type $[Co_yCu_{(1-y)}][Cr_xAl_{(1-x)}]_2O_4$.

Since the liquid phase is produced in this system already at $T = 1240°C$ (the melting point of Cu_2O), the combustion temperature should not exceed this value so that the catalyst has a sufficiently developed surface.

3. Results and discussions

3.1. Catalytic properties in CO oxidation reaction

The catalytic activity of the synthesized complex oxides was estimated at the temperature of 100% oxidation ($T_{100\%}$) of CO. The tests were carried out in a flow reactor with the CO concentration of up to 1% in the air and at a space velocity of 2000 h^{-1}.

The most active catalysts which were synthesized in system Cu-Cr-Al-O oxidized CO to 100% at a temperature of 220–240°C. The Co-containing catalysts, on the whole, have demonstrated higher activity so that further we shall deal with the catalysts in system Co-Cr-Al-O.

The tests have proved that activity of the catalysts depends on the synthesis regimes. All complex oxides synthesized in the high-temperature regime demonstrate low activity which is primarily explained by their small specific surface (0.01–0.1 m^2/g). The temperature of full oxidation of CO equals 280–320°C. The samples synthesized in the low-temperature regime demonstrate higher activity. As follows from Table 1, the activity of the catalysts in this system depends on the ratio of chromium and aluminium in the initial mixture (parameter x in Eq. (1)). With the increase of x, the temperature of 100% oxidation of CO becomes less, reaching its minimum at $x = 0.8$. The main phase of such a catalyst is represented by the spinel with lattice parameter $a = 0.833$ nm.

One of the reasons for the increase of the catalytic activity in transition from $CoAl_2O_4$ to $CoCr_2O_4$ may consist in the growth of oxygen mobility due to weakening of the Me–O bond in the spinels with a large content of chromium. Weakening of this bond is confirmed by the decrease of the frequency of stretching vibrations Me-O_o and Me-O_t and by the increase of lattice parameter (Table 1).

Further studies of the catalyst activity in the CO oxidation reaction were carried out with the samples synthesized at parameter $x = 0.8$. Having reduced the content of metallic Al in the initial mixture, we managed to decrease T_c in the SHS regime from 1200 to 1050°C. In this case, $T_{100\%}$ considerably dropped and comprised 160°C (Table 1). The reason for this shall be searched for in the change of the structure of the synthesized compounds.

Let us consider the spectra of samples 5 and 6 (Fig. 1). The spectrum of sample 5 contains only the absorption bands characteristic of spinel $CoCr_2O_4$ ($\nu_{Me\text{-}O_t} = 622$ cm^{-1}, $\nu_{Me\text{-}O_o} = 514$ cm^{-1}) which is indicative of a practically single-phase composition of the sample. The XPA data confirm the presence of the spinel with $a = 0.833$ nm and traces of the unreacted oxides. Relatively narrow absorption bands with pronounced maxima testify to low defectiveness of the structure of the synthesized spinel.

As concerns sample 6, the absorption bands relating to the spinels are wide, with diffused maxims, which testifies to deformation of the tetrahedral and octahedral oxygen surrounding of the metals [12]. Splitting of the absorption band of the stretching vibrations Me^{III}-O_o (555 cm^{-1}, 531 cm^{-1}, and 523 cm^{-1}) testifies to

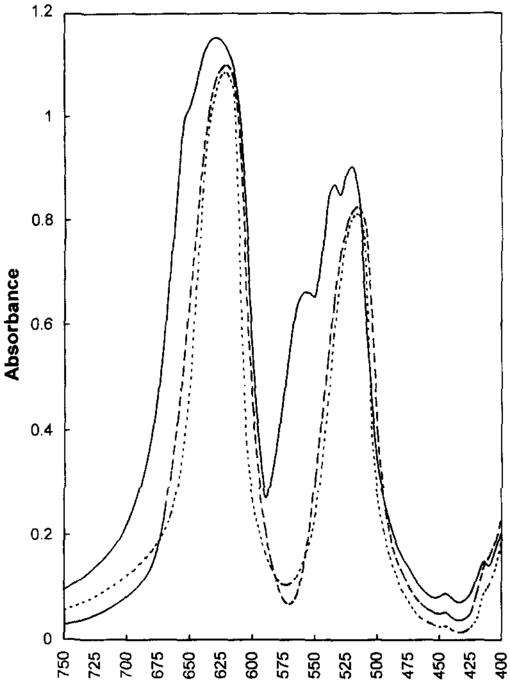

Fig. 1. IR-spectra of complex oxides $Co[Cr_xAl_{(1-x)}]_2O_4$: ---, sample 5 synthesized in the SHS regime, T_c = 1200°C; —, sample 6 synthesized in the SHS regime, T_c = 1050°C; · · ·, sample 7 synthesized in the reaction sintering regime at T = 1000°C for 3 h.

random cation distribution, i.e. to the reversal of the spinel structure, which is not characteristic of the spinel in system Co-Cr-Al-O [11]. Apart from the main spinel phase, the unreacted initial oxides are present in sample 6.

In testing samples 7 and 8, we removed metallic Al from the initial mixture and performed the synthesis of the spinels in the reaction sintering regime at T = 1000°C for 3 h. In both cases, the main phase comprised the spinel $CoCr_2O_4$ with $a = 0.833$ nm. Apart from the spinel, the samples contained the initial oxides. The IR-spectra of samples 7 and 8 are identical and contain the absorption bands of spinel $CoCr_2O_4$ ($\nu_{Me\text{-}O_t} = 622$ cm^{-1}, $\nu_{Me-O_o} = 514$ cm^{-1}) (Table 1). As compared with sample 5 these absorption bands are narrower (Fig. 1). This fact can testify to lower defectiveness of the spinel structure. These samples were less active than samples 5 and 6. The temperature of 100% oxidation of CO was 220°C.

Thus, the study of the spinel activity in CO oxidation reaction has shown the following:

1. The activity of the catalysts in system Co-Cr-Al-O depends on the ratio of Cr and Al in the spinels and increases with the increase of the chromium content.
2. The samples synthesized in the SHS regime are more active than the samples produced by reaction sintering. The lower the T_c in the SHS regime, the more defective is the structure of the synthesized spinels and, as a consequence, the higher is their catalytic activity.

3.2. Catalytic properties in hydrocarbons oxidation

The laboratory tests were conducted in a flow reactor, at a space velocity of 15000 h^{-1} and hydrocarbon concentration of 1–1.5 g/m^3. The hydrocarbons were selected for the tests proceeding from the practical tasks of purification of the industrial waste gases released in the production of the enameled wires and in the printing industry. The catalyst which demonstrated the maximum activity in CO oxidation was chosen for the tests.

Table 2 contains the data relating to oxidation of some hydrocarbons. The tests involved individual components and mixtures modelling the varnishes and paints used in the production. As follows from Table 2, the solvent vapors

Table 2
Catalytic activity of SHS-prepared $Co[Cr_xAl_{(1-x)}]_2O_4$ complex oxides in hydrocarbon oxidation reactions

Hydrocarbon	Inlet concentration (g/m^3)	Temperature of 100% conversion (°C)
Ethyl acetate	1.16	275
Butyl alcohol	0.66	300
Isopropyl alcohol	0.86	290
Toluene	1.07	300
Butyl acetate	0.93	275
Isobutyl acetate	1.50	250
Xylene	1.20	300
Methylethylketone	1.00	285

Table 3
Operating conditions for catalysts of enamelling machines

	Catalyst volume (m^3)	Hydrocarbon inlet concentration (g/m^3)	Temperature (°C)	Space velocity (h^{-1})
Stage 1	0.065	5–8	350–450	20000
Stage 2	0.12	0.5	230–300	10000

were almost fully oxidized at a temperature up to 300°C. In the practical use of the catalysts in the purification plants in Russia, it is commonly considered that the catalyst activity is adequate if the degree of purification is not less than 90% at $T = 300°C$ and space velocity of 15000 h^{-1}. Therefore, the catalysts described in the present publication can be used for purification of the industrial waste gases containing CO and hydrocarbon gases.

The commercial tests of the catalysts were carried out in the wire enamelling machines employed in the cable making industry. For satisfaction of the efficiency and pressure loss requirements placed to the catalysts, we have developed the technology for manufacture of the catalysts in the form of honeycomb units with the following geometric parameters: cell dimensions along the axes 2×2 mm, wall thickness 0.25 mm. The overall dimension of the units are from 36×36 mm to 118×118 mm. The surface-to-volume ratio of such catalysts was 19 cm^2/cm^3. The honeycomb units were molded by extrusion from the mixture of the initial powders, while the final phase composition of the units was formed during their heat treatment in the SHS regime. The units possessed adequate strength allowing for their use in the stationary catalytic purification plants.

The manufactured catalytic units were placed in standard (for the enamelling machines) stainless steel containers measuring $300 \times 600 \times 80$ mm and installed in the main technological units of the enamelling machine (1st stage) and in the afterburner (2nd stage). Such catalysts were used instead of the Pd-containing catalysts comprising Pd applied to a Ni-Cr wire or band. The catalyst operating conditions are specified in Table 3.

The concentration of the solvent vapors at the inlet of the 1st stage cannot be metered with the use of the instruments because of the design peculiarities of the enamelling machine but the calculations show that the concentration can be as high as 5–8 g/m^3, depending on the operation conditions of the enamelling machine. The efficiency of the 1st stage catalysts was estimated with respect to the quality of the wire being enameled as well as with respect to the composition and concentration of the gases re-

Table 4
Hydrocarbon concentration in flow gas line before and after afterburner

Hydrocarbon	Hydrocarbon inlet concentration (mg/m^3)	(%)	Hydrocarbon outlet concentration (mg/m^3)	(%)	Conversion (%)
Not identified	15.1	5.8			99.9
Methoxyethanol	15.1	5.8	2.2	11.7	85.4
Methoxybutanol	32.5	12.5	2.8	14.9	91.4
Methyldiglycole	35.8	15.3			99.9
Methylethylbenzene	33.6	13.6	5.0	26.6	85.1
Three methylbenzene	35.3	13.6	5.0	26.6	85.8
Dimethyl ethers of carboxylic acids	67.7	26.0			99.9
Dimethylphthalate	21.3	8.1	3.8	20.2	82.2
Σ	256.5		18.8		92.7

leased at the 1st stage outlet. In conformity with the technical requirements, the concentration of the hydrocarbons at the outlet of the 1st stage catalysts shall not be over 0.5 g/m^3.

The data contained in Table 4 refer to the composition of the gases at the outlets of the 1st and 2nd stages. The gas analysis was made by the chromatograph–mass-spectrometric method. It is evident from Table 4 that at the outlet of the 1st stage the gas composition consists mainly of aromatic hydrocarbons, esters, methyldiglycol, and its derivatives. The gas composition substantially differs from the composition on the initial varnish which is evidently explained by the differences in kinetics and mechanism of oxidation of the varnish components on the catalyst. Besides, it follows from Table 4 that the total concentration of hydrocarbons at the outlet of the 2nd stage less than 20 mg/m^3 which complies with the requirements placed by the sanitation services to such plants.

After one year of operation, the catalysts were extracted from the enamelling machine and examined. No changes in the structure and activity were detected. Presently, the honeycomb catalysts described in the present publication are manufactured by the orders of the cable making plants for their use in the enamelling machines.

References

[1] J.J. Spivey, Ind. Eng. Chem. Res., 26 (1987) 2165.

[2] A.D. Reay, in Pilvachi and A. Petros, Editors, Proc. Int. Conf. Energy Effic. Process Tecnol., Elsevier, London, 1993, p. 849.

[3] A.K. Neyestanaki and L.E. Lindfors, Combust. Sci. Technol., 97(1/3) (1994) 121.

[4] F. Severino and J. Lane, Proc. 1st Eur. Congr. Catal. Europacat 1, Mountphellier, 12–17 September 1993, Vol. 2, p. 639.

[5] V. Mathieu-Deremince, J.B. Magy and J. Verbist, Proc. 1st Eur. Congr. Catal. Europacat, Mountphellier, 12–17 September 1993, Vol. 2, p. 789.

[6] A.G. Merzhanov, in Z.A. Munir and Holt, Editors, Combustion and Plasma Synthesis of High-Temperature Materials, VCH, New York, 1990, pp. 1–53.

[7] G.G. Gladun and J. Self-Propag. High-Temp. Synth., 3(1) (1994) 58.

[8] Yu.V. Tyurkin, L.A. Chesalov and E.N. Luzhkova, React. Kinet. Catal. Lett., 58(2) or 59(1) (1996) in press.

[9] Yu.V. Tyurkin, Yu.M. Mosin, L.A. Chesalov, Proc. Int. Seminar Monolith Honeycomb Supports and Catalysts, St. Petersburg, 19–22 September 1995, Vol. 2, p. 104.

[10] Yu.V. Tyurkin, L.A. Chesalov, N.P. Antsiferova, P.P. Nikitin and I.I. Abramenko, Proc. Int. Seminar Urgent Problems of The Catalysts Manufacturing and The Large-Scale Application of Catalysis, St. Petersburg, 13–16 September 1994, Vol. 1, p. 91.

[11] J. Blasse, in B.E. Levin, Editor, Crystal Chemistry And Some Magnetic Properties of Mixed Metal Oxides with Spinel Structure, Russian Edition, Metallurgy, Moscow, 1968, p. 184.

[12] P.D. Yurchenko, Editor, Modern Vibrating Spectroscopy of Inorganic Compounds, Nauka, Moscow, 1990, p. 200.