Regularities of formation and catalytic properties of supported cobaltites in the oxidation of CO and hydrocarbons and in the reduction of nitrogen oxides

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The catalytic properties of supported cobaltites MCo_2O_4 (M = Cu, Mn, Zn, Mg) in the oxidation of CO, C_3H_6, and ethylbenzene and reduction of nitrogen oxides were investigated. The catalytic activity depends on the calcination temperature and the nature of the cation. The regularities of formation and the state of the surface of the catalysts were studied by IR spectra and diffuse reflectance spectra in the UV and visible regions.

Key words: catalytic oxidation, nitrogen oxide reduction, cobaltite, carbon monoxide, propylene, ethylbenzene.

The problem of removal of pollutants from exhaust gases has shifted emphasis on catalytic research toward the development of bifunctional catalysts active both in CO and hydrocarbon oxidation and, simultaneously, in the reduction of nitrogen oxides. Of materials containing no platinum-group metals, complex oxides with the spinel structure are promising catalysts for the elimination of pollutants from exhaust gases. The activity of spinels in oxidation is due to the presence in their structure of active oxygen and oxygen vacancies, acting as centers of activation of the gas-phase oxygen.[1-4] Previously,[5] it has been shown that spinels of some metals are active in the oxidation of CO and ethylbenzene.

The purpose of this work is to study the regularities of the formation of supported cobaltites synthesized at different temperatures and to perform comparative analysis of their catalytic properties in the oxidation of CO, C_3H_6, and ethylbenzene and in the reduction of nitrogen oxides. The cobaltites studied had the composition $MCo_2O_4/\gamma\text{-}Al_2O_3$ (M = Cu, Mg, Zn, Mn).

Experimental

The catalysts were prepared by impregnating $\gamma\text{-}Al_2O_3$ (IC-02-200) with a solution containing equimolar amounts of $Co(NO_3)_2$ and the nitrate of the required metal. After drying, the mixture was heated to 350, 500, and 700 °C and kept at each temperature for 6 h.

Bulk spinels were prepared by thorough mixing of equimolar amounts of the corresponding nitrates. The mixture was dried for 1 h at 150 °C and then heated for 6 h at 500 °C. According to X-ray diffraction analysis, in addition to spinels, the catalysts contained minor amounts of individual oxides. The presence of spinel structures was confirmed using IR spectra, based on the presence of two characteristic bands in the 400—700 cm^{-1} range.

Catalytic oxidation of CO and C_3H_6 was carried out in a flow-type reactor at a flow rate of 900 h^{-1}. The reaction mixture contained 5—6% CO (or C_3H_6) and 94—95% air. The reaction products were analyzed by GC (heat conductivity detector, He as the carrier gas, 1-m-long column packed with 5A molecular sieves (for determination of CO) or with polysorb (for determination of CO_2)).

Ethylbenzene oxidation was studied in a flow-type reactor using a KL-1 setup (Special Design Office, Institute of Organic Chemistry, Moscow). The concentration of ethylbenzene was $1 \cdot 10^{-4}$ mol L^{-1}, the flow rate was 6000 h^{-1}. The concentration of ethylbenzene was determined by chromatography using a procedure reported previously.[5]

Nitrogen oxide reduction was performed in a flow-type reactor at a flow rate of 2000 h^{-1}. The reaction products were analyzed by GC (a 3-m column packed with polysorb, 80 °C).

Diffuse reflectance spectra in the visible and UV regions were recorded on a Specord M-40 spectrophotometer and IR spectra were measured on a Specord M-80 spectrophotometer.

Results and Discussion

The formation of the catalysts was monitored by recording IR spectra and diffuse reflectance spectra in the visible and UV regions at every stage of preparation, namely, after drying and after keeping at 150, 350, 500, and 700 °C. It can be seen in the IR spectra of copper cobaltites (Fig. 1, *a*) that the bands at 570 and 670 cm^{-1}, typical of a spinel structure,[6] appear even at 150 °C. As the temperature increases, these bands become stronger, indicating an increase in the content of spinel in the catalysts. The high-frequency band is attributed to the vibrations of metal atoms (M) occurring in tetrahedral coordination with oxygen atoms. The low-frequency band is due to the vibrations of Co atoms located in octahedral vacancies of the spinel. The temperature range in which a spinel structure is formed depends on

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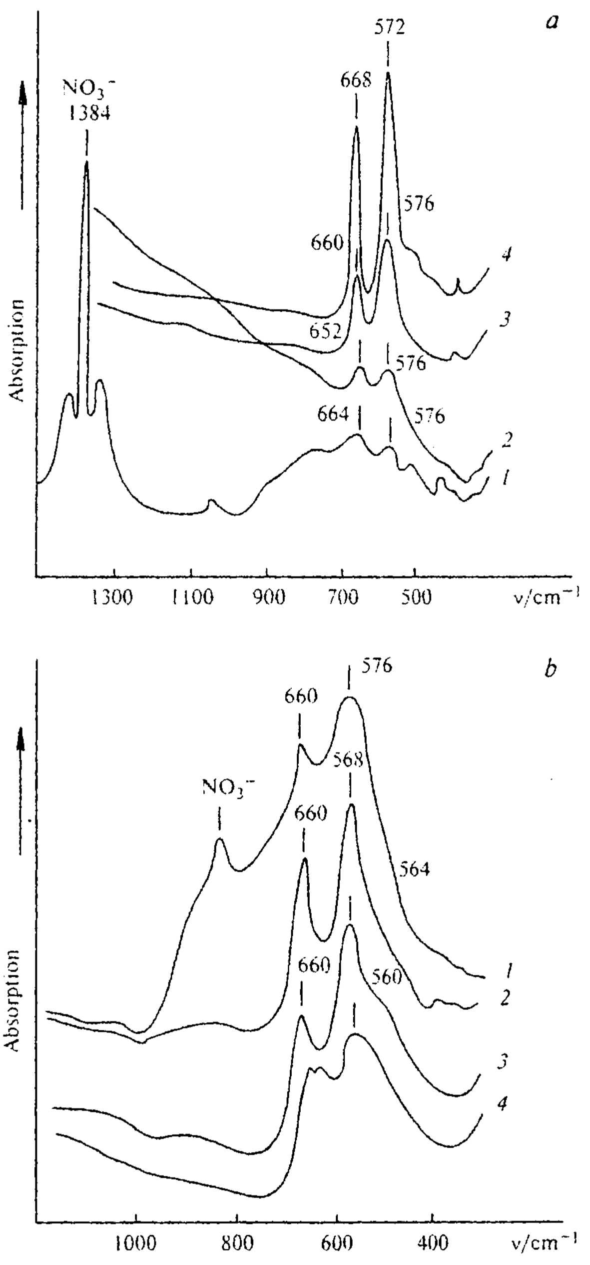

Fig. 1. IR spectra of $CuCo_2O_4$ (*a*) and $MnCo_2O_4$ (*b*) after calcination at 150 (*1*), 350 (*2*), 500 (*3*), and 700 °C (*4*).

the cobaltite composition. Thus in the case of $CuCo_2O_4$, the most intense "spinel" bands are observed at 700 °C. In the case of $MnCo_2O_4$, the most clearly defined "spinel" bands appear upon heating to 350 °C (Fig. 1, *b*). On further heating, the shape of the bands changes, pointing to either a distortion or partial destruction of the spinel lattice. The IR spectra of zinc and magnesium cobaltites also contain two bands at 580 and 660 cm^{-1}. The highest intensity of these bands is observed when the samples are heated to 500 °C. The treatment of samples at higher temperatures results in a distorted spectrum. Thus, the formation of zinc and magnesium cobaltites is accomplished at 500 °C, while at higher temperatures, the spinel structure might partially collapse.

The state of the surface of the supported cobaltites was studied using diffuse reflectance spectra in the visible and UV regions. The amounts of complex oxides supported on γ-Al_2O_3 were 1 and 3%. At higher concentrations of supported complex oxides, it is impossible to record the reflection spectra due to the considerable absorption of radiation by the sample. This is exemplified by the spectrum of $MgCo_2O_4$/γ-Al_2O_3 shown in Fig. 2. After impregnation of the support with the appropriate salts, one band at 212 nm, corresponding to the NO_3^- ion, appears in the spectrum. On heating, the intensity of this band decreases; this band disappears at 500 °C in the spectrum of $MgCo_2O_4$ and at 350 °C in the case of $CuCo_2O_4$. This points to the complete decomposition of the nitrates. Heating the sample to >200 °C brings about a band at 245 nm, which can be identified as a charge transfer band.[7] The presence of this band is attributed to the transfer of an electron from an orbital of oxygen to an orbital of the metal. Two broad bands in the visible region typical of a spinel structure were recorded upon introducing 3% of a complex oxide to the support. It can be seen in Fig. 2 that the spectrum of the 3%$MgCo_2O_4$/γ-Al_2O_3 catalyst exhibits "spinel" bands with maxima at 425 and 690 nm, which is consistent with the published data.[7,8] A finer structure of the bands in the 500—700 nm region could be detected in the spectra of samples containing 1% complex oxides. Each supported cobaltite exhibited bands at 550, 580, and 630 nm; their intensity increased when the heating temperature was raised to 700 °C. Further increase in temperature induced no changes. Comparison of the results with published data led to the conclusion that these bands indicate the presence of Co^{3+} ions in an octahedral environment.

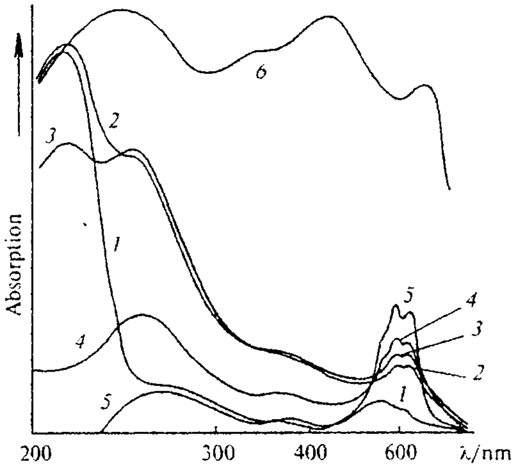

Fig. 2. Diffuse reflectance spectra of 1%$MgCo_2O_4$/γ-Al_2O_3 at 25 (*1*), 230 (*2*), 350 (*3*), 500 (*4*), and 700 °C (*5*) and 3%$MgCo_2O_4$/γ-Al_2O_3 at 500 °C (*6*).

The comparative catalytic activity of the supported cobaltites in oxidation was assessed from the temperatures needed for 100% conversion in CO and ethylbenzene oxidation and for 50% conversion in propylene oxidation. Table 1 presents data on the activity of cobaltites synthesized at 350, 500, and 700 °C in oxidation reactions. It can be seen that the catalytic activity of cobaltites depends on both the nature of the cation (metal M) and the temperature of calcination, which determines the amount of spinel formed. Matching of the catalytic activity to the optical spectra demonstrates that complex oxide starts to display catalytic activity even at an initial stage of spinel formation, *i.e.*, at 350 °C. However, no linear correlation between the activity and the spinel content can be traced. Calcination at 700 °C decreases the catalytic activity of spinel with respect to that of a sample pretreated at 500 °C. However, an increase in the calcination temperature from 500 to 700 °C enhances the intensity of the IR bands. This is due to the fact that, at a reasonably high temperature, cobalt ions can diffuse into the alumina lattice to give the spinel $CoAl_2O_4$. We monitored this process by recording IR spectra for the $Co(NO_3)_2/Al_2O_3$ system. At 700 °C, cobalt aluminate is formed, whose activity in oxidation is lower than that of cobaltites. Therefore, the activity of $CuCo_2O_4/Al_2O_3$ decreases when the calcination temperature is raised to 700 °C, although the total content of spinel increases, due to the formation of $CoAl_2O_4$ (see Fig. 1, *a*). Virtually all cobaltites reach the highest activity when calcined at 350 and 500 °C. As the heating temperature increases to 700 °C, the activity of the catalysts diminishes.

X-Ray diffraction data and IR spectra indicate that Mg, Zn, and Cu aluminates are not formed at 700 °C.

Table 1. Catalytic activity of γ-Al_2O_3-supported cobaltites in oxidation

Catalyst	T_{cal}[a] /°C	T_{conv}[b]/°C		
		CO (α = 100%)	C_3H_6 (α = 50%)	ethylbenzene (α = 100%)
20%$CuCo_2O_4/Al_2O_3$	350	90	195	265
	500	90	130	267
	700	180	200	295
20%$MnCo_2O_4/Al_2O_3$	350	170	150	271
	500	170	170	275
	700	150—160	170	293
20%$ZnCo_2O_4/Al_2O_3$	350	210	190	295—305[c]
	500	210	240	310[c]
	700	320	>400	310[d]
20%$MgCo_2O_4/Al_2O_3$	350	205	240	310[e]
	500	190	280	310[f]
	700	320	360	310[g]

[a] The calcination temperature.
[b] The temperature needed to attain a conversion degree of α.
[c] α = 66%. [d] α = 4%. [e] α = 99%.
[f] α = 60%. [g] α = 7%.

Apart from the pretreatment temperature, the nature of the cation (metal M) also influences the activity of cobaltites (see Table 1). Oxidation of CO, C_3H_6, and ethylbenzene proceeds most easily over $CuCo_2O_4/\gamma$-Al_2O_3, the activity of $MnCo_2O_4$ is lower, and $MgCo_2O_4/\gamma$-Al_2O_3 and $ZnCo_2O_4/\gamma$-Al_2O_3 show the lowest activity. This activity series is consistent with the results of investigation of bulk cobaltites.[5] Evidently, a bulk phase of the complex oxide with a spinel structure active in this type of reaction is formed on the support surface; low-activity Co aluminate is formed on all catalysts in approximately equal amounts. Thus, the presence of ions of two transition elements increases the catalytic activity of spinels in CO and hydrocarbon oxidation.

The activity of supported cobaltites in the reduction of nitrogen oxide was studied using both model mixtures and real exhaust gases containing N_2, O_2, CO, CO_2, NO_x, CH_4, and H_2O. In the presence of oxygen and steam, several reactions can take place in exhaust gases, for example,[1,9]

$$2\,CO + O_2 \rightarrow 2\,CO_2,$$

$$2\,CO + 2\,NO \rightarrow 2\,CO_2 + N_2,$$

$$CO + H_2O \rightarrow CO_2 + H_2,$$

$$2\,H_2 + 2\,NO \rightarrow 2\,H_2O + N_2,$$

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O.$$

The relationship between the reaction rates depends on the oxygen and CO concentrations. With excess oxygen, oxidation of CO and CH_x are the predominant

Table 2. Reduction of NO_x to N_2 over supported cobaltites

Catalyst	T_{cal}* /°C	Degree of NO_x conversion (%) at various temperatures (°C)			
		150	200	250	300
$CuCo_2O_4$	350	25	30	31	31
	500	27	40	49	49
	700	20	30	40	47
$MnCo_2O_4$	350	24	27	29	29
	500	45	66	77	80
	700	42	53	57	58
$ZnCo_2O_4$	350	30	40	47	51
	500	49	52	54	54
	700	18	23	26	27
$MgCo_2O_4$	350	12	18	24	30
	500	26	33	35	36
	700	23	28	32	34

Note. Exhaust gas composition: 0.9% O_2, 2.0% NO_x, 83.5% N_2, 13.6% CO (without CH_x and H_2O).
* The calcination temperature.

Table 3. Dependence of the degree of conversion (α) of NO_x and CO on the composition of the reaction mixture over 10% $CuCo_2O_4/\gamma\text{-}Al_2O_3$

Number of specimen	Composition of the gas mixture (%)	T_{exp} /°C	α (%)	
			NO_x	CO
		Model mixtures		
1	O_2 (9.8),	150	16	91
	N_2 (88.8),	200	18	99
	NO_x (0.5),	250	19	100
	CO (0.6)	300	19	100
2	O_2 (1.3),	150	56	71
	N_2 (66.5),	200	62	73
	NO_x (0.2),	250	65	74
	CO (32.0)	300	66	75
3	O_2 (0.7),	150	46	78
	N_2 (86.8),	200	53	91
	NO_x (0.4),	250	54	96
	CO (12.0)	300	54	99
		Real exhaust gas		
4	O_2 (5.2),	150	40	55
	N_2 (64.7),	200	55	83
	NO_x (1.4),	250	61	100
	CO (8.4)	300	64	100

processes, whereas at low oxygen concentrations, reduction of NO_x with CO begins. The reduction of NO_x is not influenced by the presence of CO_2, while water can decrease the catalytic activity.

In the presence of any of the cobaltites studied, NO_x is reduced to N_2. Table 2 presents data on the degree of conversion of NO_x at several temperatures over different cobaltites. It can be seen that the catalyst activity depends on both the nature of the cation and the calcination temperature, which, in turn, influences the amount of spinel formed. The catalysts calcined at 500 °C show the highest activity. An increase in the pretreatment temperature to 700 °C decreases the activity. Apparently, as in the case of oxidation, the decrease in the catalytic activity is associated with the reaction of cobalt oxide with the lattice of the support.

Analysis of the data of Table 2 shows that the nature of the cation influences the degree of NO_x conversion; in some cases, the degrees of conversion differ by a factor of two.

It is worthy of note that varying the composition of exhaust gases changes the degrees of conversion of both CO and NO_x. At higher concentrations of oxygen, the degree of CO conversion to CO_2 increases, while the degree of NO_x reduction to N_2 decreases (Table 3).

Thus, our study showed that cobaltites having a spinel structure can be regarded as bifunctional catalysts capable of accelerating both hydrocarbon and CO oxidation and NO_x reduction.

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