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Study on the thermal stability of a high Co-oxide used as low-temperature catalyst and oxidant for complete oxidation

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Abstract

A new higher Co-oxide has been synthesized. Its features are presented by means of IR-spectroscopy, X-ray analysis, XPS-spectroscopy, EPR, magnetic measurements and chemical analysis in a separate paper by the present authors. On the grounds of the obtained results the following formula, determining the content of the higher Co-oxide, has been put forward: $Co_{1-x}^{+2}Co_{x}^{+4}O_{y^{*}}(OH)_{y} \cdot mH_2O$, with the Co-ions being in their highest oxidation degrees (i.e. +4) and in an octahedral position. The synthesized Co-oxide system can be utilized as an active phase of a low-temperature catalyst as well as a strong oxidant for a complete oxidation in liquid and gas mediums.

The present paper also studies the thermal stability of the synthesized Co-oxide system by means of thermal analysis, IR-spectroscopy, X-ray and chemical analysis. The results show that both the freshly obtained higher Co-oxide and the thermally treated (up to 250°C) samples maintain their composition, structure and activity in the oxidation processes. Heated at temperature above 250°C, the Co-oxide system undergoes changes in its composition and structure, turning it into a cobaltite with a spinel structure. This is the reason for the sharp decrease of the activity of the studied system in the oxidation processes.

Keywords: Cobalt oxide; Low-temperature catalyst; Oxidation of phenol; Thermal analysis; Thermal stability

1. Introduction

Thermal stability is an important characteristic of the Co-oxides applied as catalysts in reactions of complete oxidation [1–5]. Since these processes are exothermic, the temperature of the catalyst layer is sharply increased. This phenomenon could alter the specific area as well as the composition of the catalyst and hence its activity.

The thermal stability of Co-oxides of a spinel structure has been studied by a number of authors [6–8]. It has been proved that thermal stability depends on the composition of the cobaltites as well as on the method of their synthesis [6,9]. Our previous paper dealt with a method for preparation of a high Co-oxide with composition and structure different from that of the known cobaltites [10]. Our preliminary investigations have proved the catalytic activity of this Co-oxide system in reactions of ecological importance, namely, oxidation of alcohols, aldehydes, S^{2-}, CN^{-}, etc.

The present paper aims at studying the thermal stability of a Co-oxide catalyst with a view to applying it for the purpose of complete oxidation.

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2. Experimental

The Co-oxide system was synthesized by a precipitation method. A 10% solution of $Co(NO_3)_2{\cdot}6H_2O$ and NaOH and 9% solution of NaOCl were used throughout the synthesis. NaOH was used as a precipitating agent, instead of NH_4OH, in order to avoid the formation of water-soluble Co(II) ammonia complexes. The precipitation was carried out at 70°C under constant stirring through addition of the $Co(NO_3)_2{\cdot}6H_2O$ solution to the NaOH solution. This order of addition of the reagents is essential for preventing the formation of basic nitrates. The $Co(OH)_2$ precipitate was allowed to stay in the mother liquor for ca. 30 min and then the NaOCl solution was introduced. The resulting black precipitate was allowed to stay for another 3 to 4 h. Then it was filtered, washed with distilled water until negative reaction for NO^{3-} and Cl^-, and dried at ambient temperature. This final Co-oxide system was denoted as Sample 1 (Co-fresh). The $Co(OH)_2$-precursor treatment with a strong oxidant causes two effects with major impact on the catalysts for complete oxidation:

- the oxidizing state of the metal cations is increased;
- high concentration of ion oxygen formations O^-, O^{2-}, O_2^-, i,e, 'active' oxygen is achieved on the surface of oxide and is the cause for the oxidation catalysis.

In the present paper, we shall denote an 'active' oxygen with the O^* symbol.

Sample 1 was further heated at 90°, 200°, 300° and 900°C, respectively, for 2 h to produce Sample 2 (Co-90), Sample 3 (Co-200), Sample 4 (Co-300) and Sample 5 (Co-900).

The changes in the composition and in the structure of the thermally treated Co-oxide were studied by IR-spectroscopy, X-ray analysis, thermal and chemical analytical methods. Data obtained were compared with that of a reference sample of Co_3O_4 (E. Merck, Germany), analyzed by using the same methods.

The 'active' oxygen content in the samples was determined iodometrically [11].

The differential thermogravimetry (DTG), differential thermal analysis (DTA) and thermogravimetry (TG) curves were taken with a Derivatograph Q in air, under the following conditions: mass of the sample 0.1 g, sensitivity 0.5 mV for DTA, 1.8 mV for DTG and 0.1 mV for TG; 20–1000°C temperature range; heating rate 10°C min^{-1}.

The X-ray diffraction patterns of the samples were obtained by means of a TUR-MA X-ray diffractometer (CoK_α-radiation, 2°).

The IR-spectra were recorded with a model 1750 Perkin–Elmer FTIR spectro-photometer in KBr tablets. The tablets were prepared according to the procedure described elsewhere [12]. The applied procedure helps in obtaining IR-spectra free from undesirable bands of adsorbed water (water may be adsorbed during mixing and pelleting).

The impact of the thermal treatment on the activity of the samples has been studied throughout the heterogeneous phenol oxidation in liquid phase, under the conditions described in [13]. The activity is featured by the degree of conversion of phenol α in %, calculated in the 120th minute from the start of the process ($\alpha_{120'}$).

3. Results and discussions

The 'active' oxygen (O^*) content (i.e. the percentage of excess oxygen above that required by the lowest stable valency state) in the studied samples is presented in Table 1. It can be seen that Sample 1 has higher O^* content (9.45%), which is more mobile and is also responsible for the heterogeneous oxidation even at 25°C. Samples Co-90 and Co-200 preserve their 'active' oxygen content regardless of the thermal treatment, in contrast to the high Ni-oxide produced according to an identical procedure which

Table 1
Amount of 'active' oxygen and activity of samples ($\alpha_{120'}$) with respect to the heterogeneous oxidation of phenol in liquid phase

Sample	Amount of 'active' oxygen O^*/		$\alpha_{120'}$/(%)
	(%)	(g at $g^{-1} \times 10^3$)	
Co-fresh	9.45	5.91	100
Co-90	8.29	5.18	100
Co-200	9.12	5.70	90
Co-300	1.49	0.93	51
Co-900	0.93	0.58	27
Co_3O_4	1.03	0.64	18

loses its 'active' oxygen at a temperature of 100°C [13]. The O^* content in Co-300 and Co-900 is sharply decreased and is of the same order as that in the reference Co_3O_4 sample ($\approx 1\%$). The decreased amount of the 'active' oxygen O^* in samples 4 and 5 deteriorates their oxidation capacity and activity in heterogeneous oxidation reactions in a liquid medium. The results in Table 1 concern the activity of these samples for heterogeneous oxidation of phenol in liquid phase at 25°C.

An identical effect was also established during oxidation of CN^-, S^{2-} etc., the results of which will be published in a separate paper.

3.1. IR-spectral studies of the Co-oxide system

Since the Co-fresh sample is an amorphous one, its IR-spectrum can provide information about the phase composition, thermal stability with respect to the formation of a spinel phase, and also about the way the oxygen is bonded to the metal ions. Selected IR-spectra are illustrated in Figs. 1–3.

The spectra of Co-fresh, Co-90 and Co-200 are identical, that is why only the spectrum of Co-fresh is presented. Comparing the IR-spectrum of Sample 1 (Fig. 1) with the IR-spectrum of the reference sample Co_3O_4 (Fig. 3), one can notice an essential deviation. The IR-spectrum of Co_3O_4 displays two distinct bands originated by the stretching vibrations of the Me–O bond [8,14]. The first band ν_1 at 571 cm^{-1} is connected with the BOB_3 vibrations in the spinel lattice, where B denotes the Co cations in an octahedral coordination, i.e. Co(III)-ions. The band ν_2 at 665 cm^{-1} is attributed to the ABO_3 vibrations, where A denotes the metal ions in a tetrahedral coordination, that is Co(II)-ions.

The IR-spectrum of Co-fresh displays only one distinct band at 586 cm^{-1}. The presence of this band (keeping in mind that the sample is amorphous) is very likely attributed to the presense of randomly oriented octahedral as well as to the fact that cobalt is situated in an oxygen octahedral environment [15]. This suggestion explains the presence of mobile oxygen participating in the oxidation reactions.

Comparing the IR-spectra of Co_3O_4 and Co-fresh one could establish an additional difference. The IR-spectrum of cobaltite (Fig. 3) does not display bands characteristic of OH-groups or of H_2O, while the appearance of a wide band at 3371 cm^{-1} associated with OH-groups bonded through hydrogen bond and/or with water could be noticed in the IR-spectrum of Co-oxide system. An additional information about the presence of water molecules is given by the band at 1620 cm^{-1}. These facts confirm that both OH-groups and water molecules are incorporated in Co-fresh, Co-90 and Co-200. Data of IR-analysis correlate with data

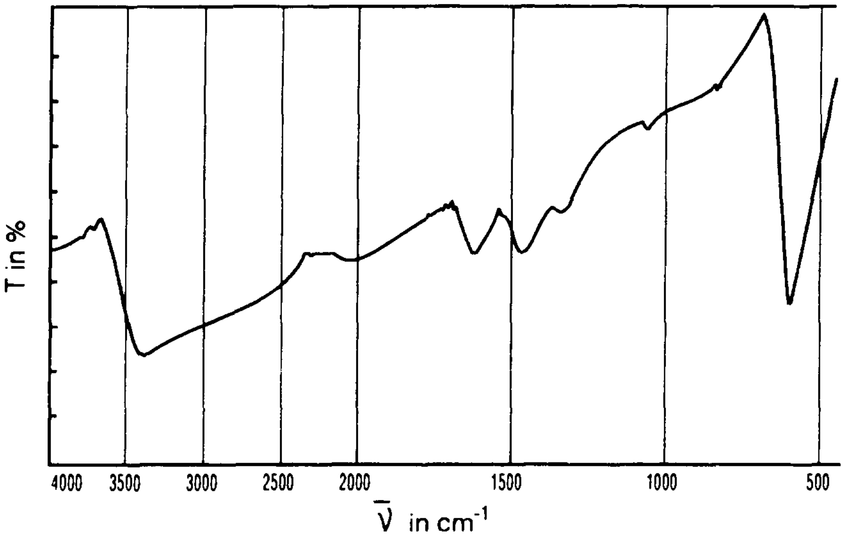

Fig. 1. IR-spectrum of Co-fresh.

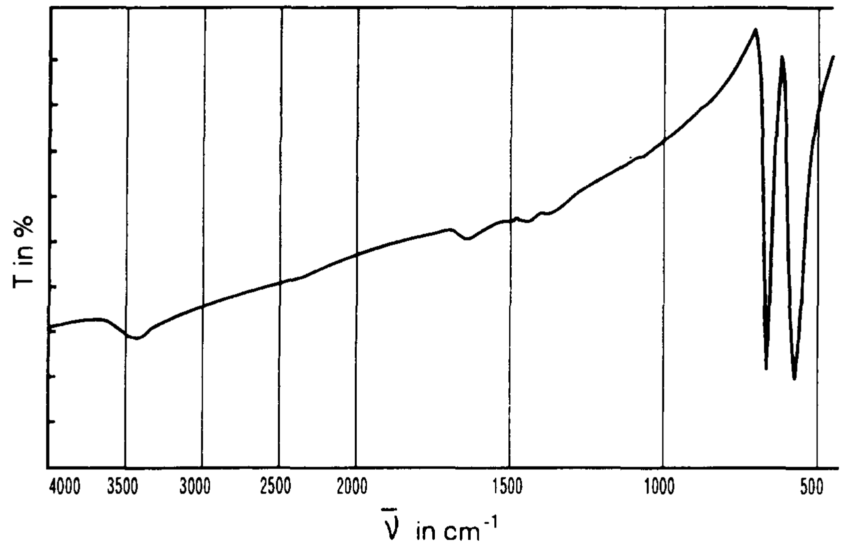

Fig. 2. IR-spectrum of Co-300.

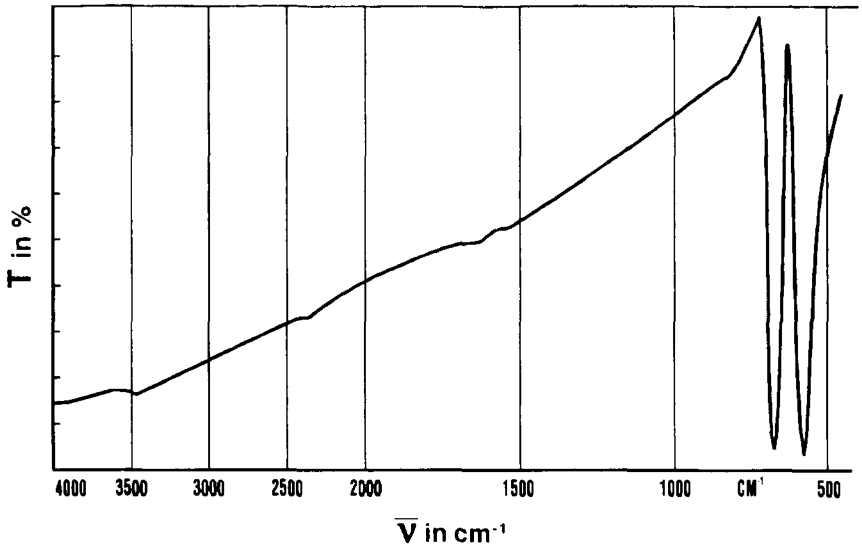

Fig. 3. IR-spectrum of Co_3O_4.

of thermal analysis. On the other hand, the comparison of the IR-spectra of the studied samples with the 'active' oxygen content in the samples reveals a correlation between the O^* content and the intensity of the band at 586 cm^{-1}.

The IR-spectrum of Co-300, as shown in Fig. 2, (the spectrum is identical to the IR-spectra of Co-900) indicates that heating of Co-fresh at temperatures exceeding 300°C initiates a spinel formation. The bands ν_1 and ν_2 characteristic of the spinel lattice appear in the IR-spectra of Co-300 and Co-900. These results point out that on heating Co-fresh at $T \geq 300°C$, a part of the octahedrally oriented Co-ions turns into tetrahedral coordination. Many authors

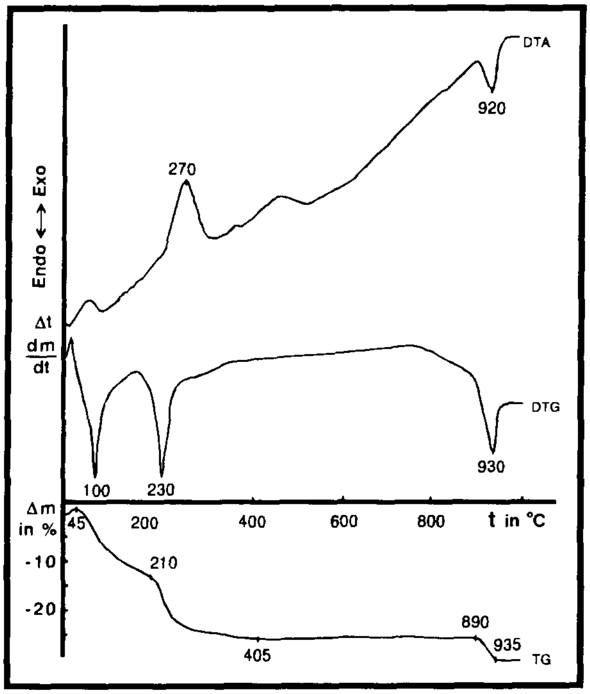

Fig. 4. Thermal analysis of Co-fresh.

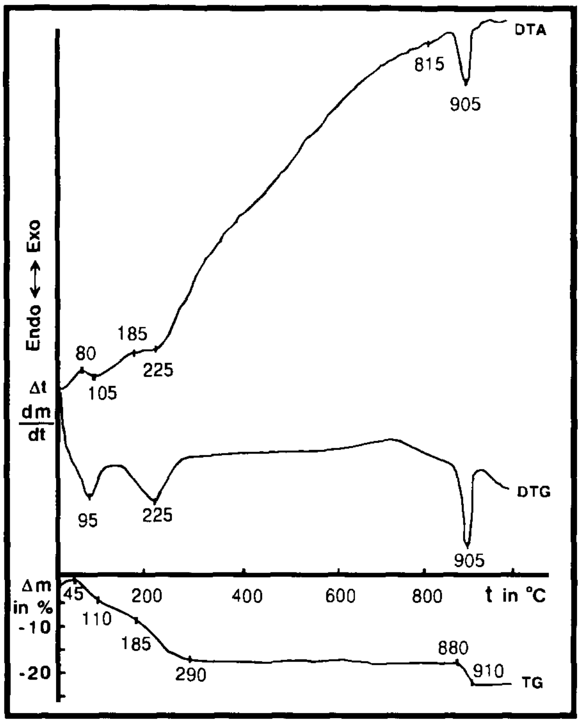

Fig. 5. Thermal analysis of Co-300.

state that the ions in the tetrahedrally coordinated sites are either inactive or only contribute a little to the overall activity in the oxidation processes [16–18]. On these grounds, one could expect Co-300 and C-900 to be less active than Co-fresh in oxidation processes, which is explained by the stronger $Me(II)^{tetr}$–O bond as compared to the $Me(III)^{oct}$–O bond.

3.2. *Thermal analysis*

DTA, DTG and TG curves of Co-fresh and Co-300 are shown in Figs. 4 and 5.

Three endo-effects are visible on the DTA and DTG curves – the first at 100° to 110°C, the second at 220° to 230°C and the third being the most distinct at 920° to 930°C.

The sharp endothermic peak at 100° to 110°C is due to the removal of physically adsorbed molecular water accompanied by a well-defined stage in the TG curves. The loss in weight between 100° and 210°C, as observed in the TG curves, is primarily due to removal of chemically bound or compositional water.

The endo-effect at 230°C is probably due to the loss of 'active' oxygen which is primarily responsible for the conversion of Co-oxide to Co_3O_4.

The third endo-effect indicates that the spinel formed at temperature above 250°C begins to decompose at 920°C, according to the following scheme:

$$Co_xCo_{3-x}O_4 \rightarrow CoO + Co_yCo_{3-y}O_4 + O_2$$

This results in CoO and a spinel phase of a composition similar to the composition of Co_3O_4 [7,8].

The DTA curve of the Co-fresh (Fig. 4) displays two exo-effects. The first distinct exo-effect is at 270°C, while the second at 450°C. Both effects are probably associated with processes of spinel formation. This conclusion is confirmed by the IR-data as well. The results of the thermal and IR-spectral analyses reveal that the synthesized Co-oxide system is transformed into cobaltite at $T > 250°C$, the produced spinel being stable up to 920°C. In the range 300° to 920°C, no effects in the DTA and TG curves were observed.

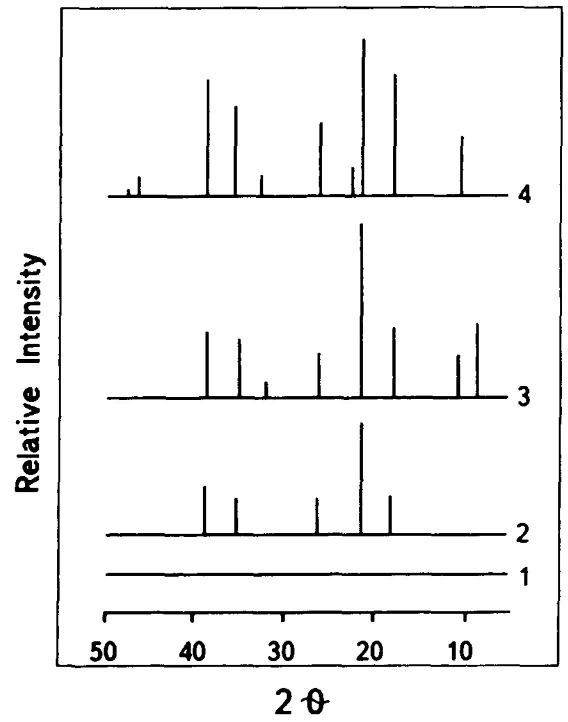

Fig. 6. X-ray diffraction patterns: 1 – Co-fresh; Co-90 and Co-200; 2 – Co-300; 3 – Co-900; 4 – Co_3O_4.

3.3. X-ray spectral analysis

All studied samples were subjected to X-ray analysis. Experimental data are listed in Fig. 6 and Table 2.

The results show that samples of Co-fresh, Co-90 and Co-200 are amorphous and their diffraction patterns differ from diffraction pattern of the reference sample (Co_3O_4). Samples Co-300 and Co-900 have a composition similar to that of Co_3O_4. Only several diffraction maxima of low intensity ($\approx$4.8%) characteristic of Co_3O_4 are absent in their spectra.

Table 2 shows the *d* spacing values in Å of the lines in the X-ray patterns and the relative intensities, *I*, in % of Co-300, Co-900 and Co_3O_4. The three diffraction patterns do not differ in positions of their characteristic diffraction maxima. There is a certain difference only with respect to the relative intensities of some peaks. From these XRD patterns it is clear that the Co-fresh, heated at temperature above 250°C, undergoes changes in its composition and structure and turns into a cobaltite with a spinel structure.

Table 2
X-ray analysis data

Θ/(°)	Co-300		Co-900		Co_3O_4	
	d/(Å)	*I*/(%)	*d*/(Å)	*I*/(%)	*d*/(Å)	*I*/(%)
18.50	2.82	35	2.83	40	2.82	54
21.80	2.41	100	2.42	100	2.43	100
26.55	2.00	27	2.01	26	2.03	32
35.40	1.545	29	1.547	34	1.545	39
39.10	1.419	34	1.419	38	1.419	50

4. Conclusions

On the basis of the results achieved in this work and having in mind our previous investigations and the data given in the works of other authors, it may be concluded that the newly synthesized higher Co-oxide may find its application as low-temperature catalyst and oxidant in the gas and liquid phases. This application is based on the following specific characteristics:

- metal ions are in their highest oxidation degree (i.e. +4), as well as in octahedral coordination;
- high content of 'active' oxygen.

The composition, structure, morphology, and activity of the featured higher Co-oxide undergo the following changes upon heating the samples at temperatures above 250°C:

- O^* is released, bringing about a decrease in the active oxide sites as well as formation of a spinel structure;
- transition from X-ray amorphous to crystal state takes place;
- the octahedrally positioned ions are taking tetrahedral coordination.

It is well known that these effects lead to reduced oxide activity in the oxidation processes.

Acknowledgements

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