

IR spectroscopic investigation of cation distribution in Zn–Co oxide catalysts with spinel type structure

G.N. Kustova*, E.B. Burgina, G.G. Volkova, T.M. Yurieva, L.M. Plyasova

Boskov Institute of Catalysis, Prosp. Akad. Lavrentieva 5, Novosibirsk, 630090, Russia

Abstract

The structure of Zn–Co spinel prepared by coprecipitation was studied by IR spectroscopy. The characteristic bands of extra OH^- and H_3O^+ groups were shown to exist in IR spectra up to 700°C . Comparing IR spectra of a poorly crystallized low temperature catalyst with that of a perfect Zn–Co spinel, we have associated the noticeable splittings and shifts of the F_{1u} bands with definite structural distortions. The presence of extra anions in the catalyst with a spinel-like structure in the temperature region $100\text{--}700^\circ\text{C}$ is the factor that stabilized the unusual cation distribution in this catalyst. The most plausible cation distribution in such a spinel is proposed as follows: Co^{3+} and Zn^{2+} are in octahedral positions, and Co^{2+} and Zn^{2+} are in tetrahedral ones. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Spinel cobaltites are widely used as environmental catalysts for the oxidation of CO [1] and hydrocarbons [2–3], thus studies of the formation, structure and cation distribution are of great interest to understanding their catalytic action. It was shown that the catalytic activity of Co catalysts with spinel type structure depends on the cation distribution [4]. In spinels synthesized at low temperature, the cation distribution differs from that of high-temperature spinels because of the incomplete removal of the anions of the precursor compounds [5]. For catalytic purposes, the spinels are usually synthesized via coprecipitation of metal cations

from their nitrate solutions by carbonates or alkali. At low temperatures ($350\text{--}550^\circ\text{C}$) the compounds are poorly crystallized according to X-ray characterization and more information about the structure can be obtained from vibrational (in part IR) spectra. In our previous paper [6] the formation of Zn–Co catalysts was investigated. This research was carried out to study the cation distribution during the formation of the Zn–Co spinel structure catalyst using IR spectroscopy.

2. Experimental

The samples (Zn:Co = 1:2 and 1.5:2) were precipitated from a solution of mixed metal nitrates by an ammonia solution at $\text{pH } 7.0 \pm 0.2$ and the temperature $70 \pm 2^\circ$. An excess of hy-

* Corresponding author.

drogen peroxide was repeatedly introduced into the mixture to oxidize Co^{2+} to Co^{3+} . The precipitates were washed from nitrates, dried at 100°C , and heated at 350 , 540 , 700 , 800 and 900°C for 24 h.

IR-spectra were obtained using Fourier Transform spectrometer IFS-113v (Bruker). The samples were prepared as a suspension in vaseline oil or by pressing with alkali metal halides. A low-temperature IR chamber (-196°C) was used to record IR spectra with necessary resolution.

3. Results and discussion

The perfect ZnCo_2O_4 spinel structure has the space group O_h^7 with eight formula units per unit cell. The Zn atoms are in tetrahedral 8a sites of point symmetry T_d ; the Co atoms are in octahedral sites 16d of point symmetry D_{3d} . Therefore, the active vibrational modes are distributed as follows: $\Gamma_v = 4F_{1u} + A_{1g} + E_{1g} + 3E_{2g}$. The four F_{1u} modes are infrared active. Four absorption bands with maxima at 670 cm^{-1} (ν_1), 582 cm^{-1} (ν_2), 392 cm^{-1} (ν_3) and 215 cm^{-1} (ν_4) [7] were observed in the IR-spectra of perfect ZnCo_2O_4 . The frequencies ν_1 and ν_2 are assigned to the F_{1u} vibrations of the octahedral groups, the frequencies ν_3 and ν_4 correspond to the F_{1u} vibrations of both tetrahedral and the octahedral groups; major contributions of the octahedral and tetrahedral groups being to ν_3 and ν_4 , respectively.

Four absorption bands with maxima at 660 – 680 , 570 – 605 , 375 – 390 and 202 – 210 cm^{-1} were observed in the IR spectra of the samples dried at 100°C and calcined at 540°C , 700°C , 800°C and 900°C (Fig. 1). These bands are characteristic of the Zn–Co spinel structure and correspond to the above mentioned ν_1 , ν_2 , ν_3 and ν_4 frequencies. Therefore, a spinel-like structure is observed immediately after the precipitation prior to calcination of the samples. The ν_1 , ν_2 , and ν_4 bands are split and asymmetric, in addition, ν_4 (202 cm^{-1}) is consider-

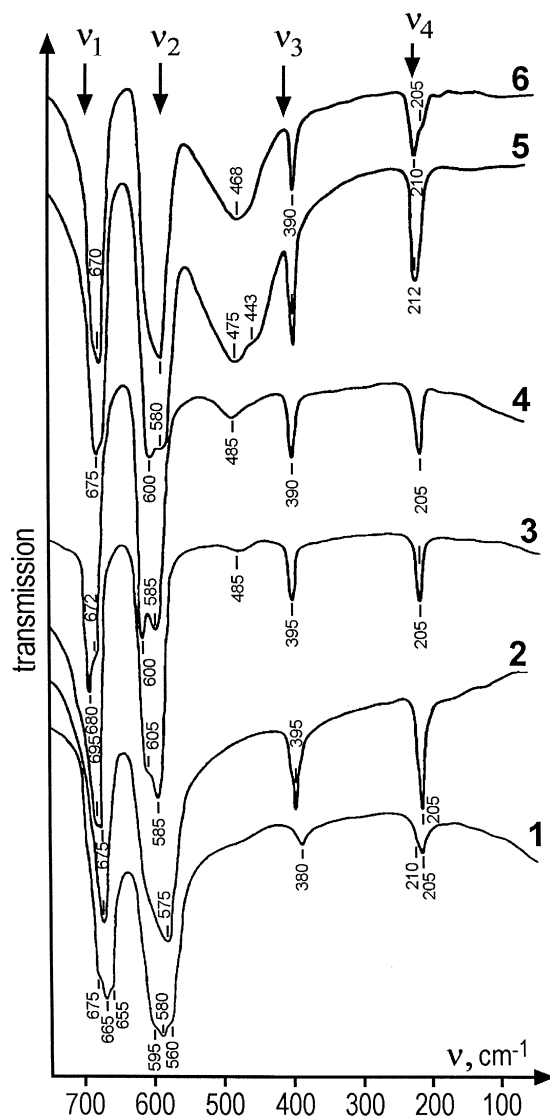


Fig. 1. IR spectra of ZnCo_2O_4 calcined at different temperatures: (1) 100 , (2) 540 , (3) 700 , (5) 800 , (6) 900°C ; and (4) $\text{Zn}_{1.5}\text{Co}_2\text{O}_4$ calcined at 700°C .

ably shifted to a lower frequency in comparison to the position of the normal spinel. The bands at 1150 , 1730 , 3320 – 3600 cm^{-1} were registered in IR spectra of these samples (Fig. 2). These bands were attributed to H_3O^+ and OH^- ions in accordance with literature data [8] and our ab initio calculation [9]. We suppose that H_3O^+ ions occupy some sites in the catalyst structure. The intensities of the peaks decrease with increasing calcination temperature. The

complete disappearance of these extra ion bands in the spinel spectra is observed for the sample calcined at 700°C.

The splitting and asymmetry of the spinel F_{1u} absorption bands are attributed to the presence of different cations located at the same crystallographic positions [10]. Thus, the data obtained allow us to suggest that both Co and Zn cations are located in octahedral as well as in tetrahedral positions of the spinel structure. The IR spectra of the Zn–Co sample with an excess of zinc (Zn:Co = 1.5:2) (Fig. 1, curve 4) confirms the preference of zinc cations to be located in octahedral sites. In this case, the octahedral bands, ν_1 and ν_2 (670 and 582 cm^{-1} , respectively), are more split relative to the bands of the sample, Zn:Co = 1:2, at the same temperature (Fig. 1, curve 3). According to UV–VIS–DR spectra [6] and the above IR data, the following cation distribution seems to be the most plausible: Co^{3+} and Zn^{2+} are in octahedral positions, and Co^{2+} and Zn^{2+} are in tetrahedral ones.

After calcination at 800°C, a shift of the absorption band ν_4 to 212 cm^{-1} , coinciding with the band in a perfect spinel, is observed in the IR spectra (Fig. 1, curve 5). Intensities of all spinel bands increase with temperature increasing to as high as 700°C. The intensities of ν_1 and ν_2 bands stop to increase after calcination

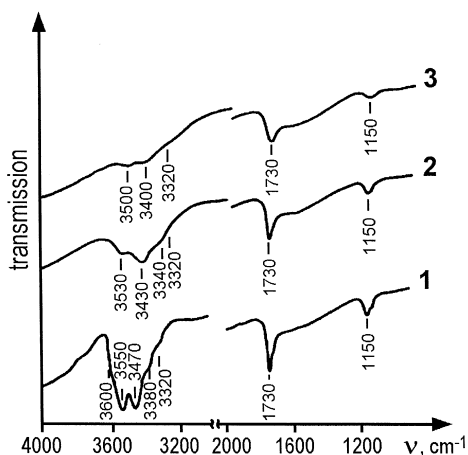


Fig. 2. IR spectra in region of 1200–4000 cm^{-1} for ZnCo_2O_4 calcined at (1) 100°C, (2) 350°C and (3) 540°C.

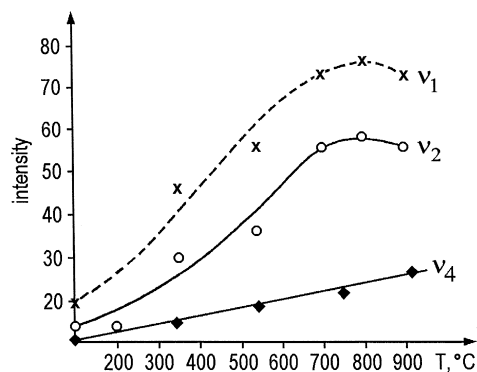


Fig. 3. The absolute intensity of the bands ν_1 , ν_2 and ν_4 as a function of the calcination temperature.

at 800°C and decrease after treatment at 900°C, whereas the ν_4 band keeps to increase (Fig. 3). It is suggested that the intensities of the bands increase up to 700°C as a result of an increased crystallinity. X-ray data confirm the formation of the perfect spinel structure at high temperature. The intensity reduction of the ν_1 and ν_2 bands at 900°C is accounted for a relative decrease of the quantity of cations in octahedral sites. At 700°C, a new band arises at 485 cm^{-1} in the IR spectra. This band is characteristic of the ZnO phase. The intensity of the ZnO band increases with temperature. The formation of zinc oxide at above 700°C is due to the removal of zinc cations from both the octahedral and tetrahedral sites.

4. Conclusions

The IR spectroscopic investigation allows us to identify a spinel-like structure immediately after the sample precipitation prior to calcination. Four absorption bands typical for the spinel structure were observed at 200–700 cm^{-1} , but the ν_1 , ν_2 and ν_4 bands were split, and the ν_4 band was shifted to a lower frequency relative to the normal spinel ZnCo_2O_4 . In addition extra bands observed at 1150, 1730, 3320–3600 cm^{-1} are attributed to H_3O^+ and OH^- ions. A defect spinel which structure contains H_3O^+ and OH^- groups is formed at 100–700°C. The presence of these extra anions in the spinel-like structure

of the catalyst is the factor that stabilizes the unusual cation distribution in temperature region 100–700°C. The removal of these extra ions and decomposition of the Zn–Co spinel occur at 700°C. Zn–Co spinel decomposes into two phases: ZnO and spinel containing less zinc cations.

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