Study of Co-Cr Mixed Oxides for Different Applications

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Mixture metal oxide system Co-Cr were prepared by decomposition of the precursor complexes obtained from a mixture Co-Cr nitrates with tartaric acid. The samples were subsequently submitted to chemical analysis, magnetic measurements, IR spectrometry, UV-Vis, thermal analysis, XRD, EXAFS and TPR. At 600°C was identificated a solid solution of $CoCr_2O_4$ with Co_3O_4. With Cu-CrK-edge EXAFS the local structure of samples calcinated of 420°C and 600°C was obtained. By theirs analysis was calculated: the lengths of M-O bounds, number of coordination (N), Debye-Waller factor (A_1) and x metallic cations fraction in tetrahedral structures (spinelic centers). The TPR measurements were emphasized the existence of two reduction cycles.

Keywords*: mixed oxides, spinelic compounds, thermoprogrammed reduction*

Mixed oxide materials are widely used as catalysts [1-5], different composites [6-9], nanomaterials templated by egg-shell membranes [10], preparation of polyamides composite nanofibres [11], preparation of ceramic and inorganic fibres [12-15], mixed oxide materials for development of integrated gas sensors [16-20], composite type multi-component metal oxide-based sensors [21-24].

Transition metal oxides are widely used as catalysts for complete oxidation of CO from exhaust gases and of VOCs (volatile organic compounds). The catalytic oxidation is the most attractive way to eliminate VOCs at low concentration in industrial gaseous effluent. For practical applications, the catalyst should be supported on a structurated support to a treat large gas flows with low pressure drop.

Several studies have investigated the catalytic oxidation as an alternative to the incineration process for the destruction of VOCs. The catalytic oxidation can be highly efficient for the total oxidation avoiding the formation of harmful byproducts. The catalytic reaction is an energy-efficient low cost process and can be carried out at much lower temperatures avoiding the formation of NOx. There have been numerous studies on the catalytic oxidation of several organic compounds using different materials based on transition metal oxides, bulky and supported, as catalysts [25-28].

This basic chemical equation of oxidation of organic molecule (HC) is:

$$HC + air\,(O_2) \xrightarrow{catalyst} CO_2 + H_2O \qquad (1)$$

The temperature needed for the catalytic oxidation process depends on the type of the organic compounds, space velocity (i.e. volumetric flow rate of gas per catalyst volume in given time) and concentration.

Transition metal oxides have shown very good achievements with respect to NO reduction. Most of the reported catalysts require o high working temperature 673-773 K, to get reasonably high NO reduction [29-32]. In the some works is presented simultaneous removal of VOCs and NOx by mixed oxides catalysts [33-36].

The aim of the present paper is to check a mixed oxides material with stability of structure, starting from complexes of Co-Cr with tartaric acid.

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Experimental part

The precursor complexes were obtained by precipitation of Cu-Cr nitrates in aqueous solution with tartaric acid at *p*H 7, in a solution of ethanol and ammonium hydroxide 10% in a ratio 1:1. After precipitation, the resulted compound was dried in vacuum at 90°C and calcined at 600°C. The sample were subsequently submitted to chemical analysis, magnetic measurements, IR spectrometry, UV-VIS, thermal analysis, XRD, EXAFS and TPR.

Magnetic measurements ESR was carried out with JEOL spectrometer and EPR with Varian spectrometer [29]. Thermal analysis were achieved with Setaram Set Sys DSC-TG/DTA Equipment and UV-Vis measurements with Perkin Elmer Lamda 35 spectrometer [29]. The structure and crystalline lens parameters of the samples were determined by EXAFS method with pHi QUANTERA SXM 2010 and XRD spectra were obtained with Rigaku last IV apparatus. The IR investigation was carried out in the spectral range 4000-400 cm^{-1} with M-80 Carl Zeiss Jena spectrometer.

Thermoprogrammed reduction (TPR) measurements was carried out with CHEMBET 3000 apparatus by determining the hydrogen consumption from a flowing gas mixture of argon with 3% hydrogen. The gas flow rate was kept at 6 $cm^3\ s^{-1}$. A linear heating program of temperature increasing was achieved in the range 20-500°C. The samples were pretreated in flowing argon at 500°C. After cooling them in flowing argon to room temperature, the carrier gas was switched to the mixture argon with 3% H_2 and baseline was stabilized; the system was then heated at 10 K/ min^{-1} to 500°C while the hydrogen consumption from the carrier gas was recorded (curve HCR_1, heating cycle record). The sample was kept at 500°C until the baseline was stable and then cooled in argon to room temperature. After switching on the gas mixture and baseline stabilization, the heating program was again applied and the curve HCR_2 was recorded.

Results and discussions

The corroboration of the results concerning chemical analysis, magnetic measurements [29] and IR-spectra to the following formula for the precursor:

$[Cr\ Co_4\ Ta_6] \cdot 5H_2O$(where Ta is the tartaric anion).

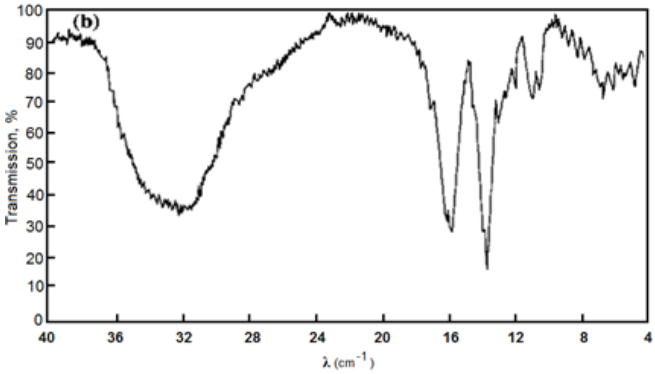

Fig.1. The IR spectra of the 4Co-1Cr-Ta precursor

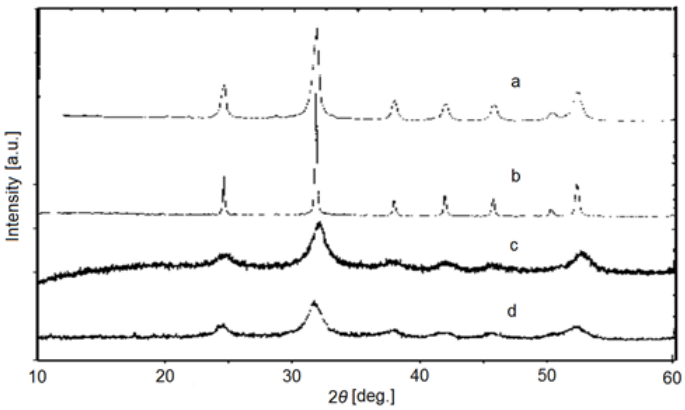

Fig.2.The XRD spectra of the 4Co-1Cr mixed oxides calcined at different temperatures: a-500°C, b-550°C, c-600°C, d-650°C

Table 1 THE CHARACTERISTICS OF IR SPECTRA OF 4Co:1Cr SAMPLE

Sample	ν(OH) R-OH R-COOH	ν(OH) H_2O	νasimetric (C-O) R-COOH	νsimetric (C-O) R-COOH	δ(OH) ν(C-O)	γ(OH) ν(C-C) δ(OH) R-OH R-COOH ν(CH3)	ν(M-O) νasim.M-O νsim.M-O
Co:Cr:Ta	3400 3100	2880 2860	1610 1580	1375	1130 1062	840 780	680 480

The transformations of the complex into oxides were checked by TGA analysis. The thermogravimetric study show that the hydration water of the complex is eliminated up to 200°C.

The decomposition of the complex has two stages:

-first, corresponding to 21% loss of weight up to 240°C;

-second stage highly exothermic ($\Delta T \cong 100$°C, $\Delta m \cong 48\%$) up to 400-420°C.

Over this temperature, the loss of mass is not recorded.

IR and electronic spectra as well as magnetic measurements have indicated that both COO^- and partially HO^- are coordinated at metallic ions in the precursor.

An IR investigation was carried out on sample in the spectral range 4000-400 cm^{-1} (fig. 1).

The main characteristic IR absorption bands are presented in table 1.

A large and intensive absorption band at 3400 - 3100 cm^{-1} is typical for stretching vibrations associated to HO^- groups (ν_{OH}). The bands at 1610-1580 cm^{-1} as well as the sharp band at 1375 cm^{-1} are usually attributed to asymmetric stretching vibration and symmetric vibration of the C-O bonds in carboxylic ion, respectively. These could be assigned to tartaric acid salts with Co-Cr metallic couple. Sharp and weak bands are found in the region 680-480 cm^{-1} which are attributed to Me-O bonds.

Also, the UV-Vis reflection spectra [29] indicated the octahedral coordination of the tartaric acid to both metallic ion. The 410 nm band of the $CrCo_4Ta_6.5H_2O$ complex was ascribed to the transition: $^4A\ 2g \rightarrow {}^4T\ 1g$ (F) within an octahedral configuration of the Cr^{III} (d^3) ion. The 535 nm peak can be explained by the superposition of the bands corresponding to the: $^4A\ 2g \rightarrow {}^4T\ 2g$ (P) of Cr^{III} (d^3) in an octahedral configuration and: $^4T\ 1g \rightarrow {}^4T\ 1g$ (P) ($\rightarrow g_3$) of Cr^{II} (d^7) in an octahedral configuration (high spin) transitions, respectively.

XRD spectra of calcined samples (fig. 2) revealed: at 500°C the crystalline lens of mixed oxides 4Co-1Cr are evidently. After increase of calcination temperature, the amount of crystalline lens compounds increases. At 600°C was identified a solid solution of $CoCr_2O_4$ with Co_3O_4. At 650°C the amount of spinelic fase ($CoCr_2O_4$) decrease owing to his decomposition.

With Cu-CrK-edge EXAFS (fig. 3 and fig. 5) and Fourier transform magnitudes spectra (fig. 4 and 6), the local structure of samples calcined of 420 and 600°C was obtained. By theirs analysis was calculated: the lengths of M-O bounds, number of coordination (*N*), Debye-Waller factor (A_1) and *x* metallic cations fraction in tetrahedral structures (spinelic centers).

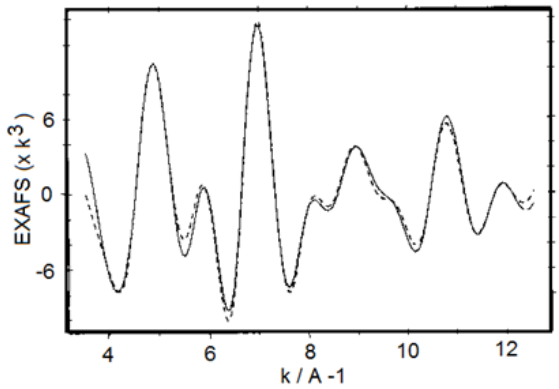

Fig.3. K-edge EXAFS spectra of 4Co: 1Cr- 420°C sample (amorphous mixed oxides) at K limit of Cr absorption: experimental - continuously line; theoretical – discontinuously line

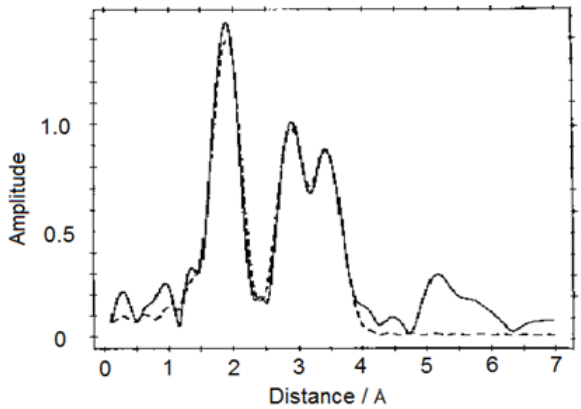

Fig.4. Fourier transform magnitudes spectra of 4Co:1Cr- 420°C sample (amorphous mixed oxides): experimental - continuously line; theoretical – discontinuously line

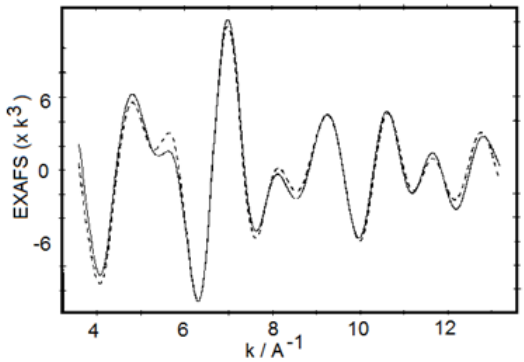

Fig. 5. K-edge EXAFS spectra of 4Co:1Cr- 600°C sample (spinelic compounds) at K limit of Cu absorption: experimental - continuously line; theoretical–discontinuously line

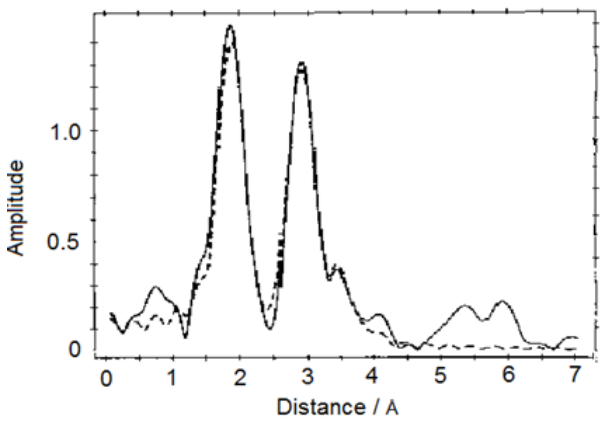

Fig.6. Fourier transform magnitudes spectra of 4Co: 1Cr- 600°C sample (spinelic compounds): experimental - continuously line; theoretical – discontinuously line

The x fraction was calculated by relation (2):

$$N_m = x\,N_{tetrahedral} + (1-x)\,N_{octahedral} \qquad (2)$$

The lengths of M-O and M-M bounds are presented in table 2 and parameters of crystalline structures in table 3, respectively.

In concordance with these data is relevant that in the sample calcined at 420°C, the spinelic phase ($CoCr_2O_4$) is not present. In the sample calcined at 600°C, this is the main phase and it is confirmed by XRD spectra.

The length of Co-O bond is 1.95-1.96 Å in the spinelic phase and 1.939 Å in the amorf mixed oxides. The length of Cr-O bond is 1.92-1.93 Å in the spinelic phase and 1.90 Å in amorf mixed oxides. This proves that the spinelic phase is a structure with defects.

Figure 7 shows the HCR_1 and HCR_2 curves (TPR measurements) for the calcined sample at 600°C. These curves show that: the hydrogen consumption in HCR_1 is 20 times higher than the corresponding consumption in HCR_2. In HCR_1 the hydrogen consumption begins at temperatures higher than 300°C, reaches its maximum at 400°C and exhibits a maximum at 480°C. In HCR_2, a significant maximum is recorded at 280°C in addition to the 400°C maximum which is still present but to a lower extent.

The existence of HCR_1 and HCR_2 show that the first heating cycle of the sample with hydrogen does not determine the total reduction. The reduction is activated and occurs in a certain time. Moreover, the sharp peak from HCR_2 at 280°C may be interpreted as oxide phases which lead to a surface reconstruction. The existence of HCR_2 is probably due to the adsorption of hydrogen on the metallic clusters that appeared during to cobalt as well as to reduction of the oxide traces (from Co_3O_4 to CoO and CoO to Co).

Table 2
METAL-OXYGEN AND METAL-METAL DISTANCES INTO STRUCTURES OF SAMPLE

Centers	Number of coordination	Type of atom	Distance(Å) (M-O) ; (M-M)
	$CoCr_2O_4$		
Tetrahedral	4	O	2.015
	8	M(6)	3.427
	4	M(6)	3.703
	8	O	3.435
	4	O	3.787
	4	M(4)	3.678
Octahedral	4	O	1.970
	2	O	2.140
	2	M(6)	2.890
	4	M(6)	3.057
	4	M(6)	3.427
	2	M(6)	3.703
	2	O	3.503
	2	O	3.689
	4	O	3.766

Table 3
PARAMETERS OF CRYSTALLINE LENS OF 4Co:1Cr MIXED OXIDE SAMPLES

Conditions	Sample	N_1	R_1 (Å)	A_1 (Å)^2
At K limit of Co absorbtion	4Co:1Cr 420°C	5.4	1.939	0.017
	4Co:1Cr 600°C	5.2	1.958	0.013
	4Co:1Cr 650°C	4.6	1.961	0.011
At K limit of Cr absorbtion	4Co:1Cr420°C	5.3	1.902	0.010
	4Co:1Cr 600°C	5.9	1.920	0.009
	4Co:1Cr 650°C	4.9	1.932	0.008

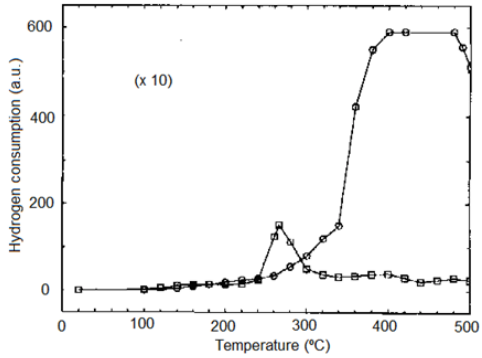

Fig.7. Hydrogen consumption in two reduction cycles for 4Co:1Cr 600°C: (Ë%) TRP_1, (¡%) TRP_2

Conclusions

Calcinated at 600°C, Co-Cr mixed oxides prepared from precursor complexes, have a stable spinelic structure. It is presented by a solid solution of $CoCr_2O_4$ with Co_3O_4.

The method of preparation from the precursor complex is suitable for this type of mixed oxides.

The TPR curves give information concerning surface reconstruction induced by the interaction of the sample with hydrogen.

The spinelic phase ($CoCr_2O_4$) have a crystalline structure with defects.

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