Study of Cu-Cr Mixed Oxides for Different Applications

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Mixture metal oxide system Cu-Cr were prepared by decomposition of the precursor complexes obtained from a mixture Cu-Cr nitrates with tartaric acid. The samples were subsequently submitted to IR spectrometry, UV-Vis, XRD, EXAFS and TPR. Calcined at 600°C, Cu-Cr mixed oxides prepared from precursor complexes, have a stable spinelic structure.

Keywords: mixed oxides, spinelic compounds

Various mixed oxides containing Cu, Cr and other metals have been obtained by the calcination of the precursors type hydroxycarbonate at different temperatures. Their characterization was carried out by thermal analysis, X-ray diffraction, infrared reflectance spectroscopy and determination of specific surface area by the BET method [1]. Species obtained by reduction of mixed oxide, determined by X-ray diffraction up to 973K, have shown that among the reducible species have been identified CuO, $CuCrO_4$ and metallic copper.

Changes of crystallographic, electrical and thermal properties of CuCr2O4 spinel were investigated by replacing Mg, i.e., $Cu_{1-x}Mg_xCr_2O_4$, Cr and Al, i.e., $CuCr_{2-x}Al_xO_4$. The variation of electrical resistivity with temperature for all tetragonal samples was similar to $CuCr_2O_4$. The thermal stability of the spinel has proven to be reduced due to the high concentration of Cu^{2+} ions tetrahedral [2].

A catalyst spinel $CuCr_2O_4$ substituted with Mg and Al was tested for carbon monoxide oxidation at atmospheric pressure and temperatures between 373 and 723K. $CuCr_2O_4$ activity of the catalysts decreased even when small quantities of Cu are replaced with Mg or of Cr with Al, but none of the substituted catalysts was not as active as $CuCr_2O_4$ [3]. The decrease in activity is due to the decrease in the active Cu^{2+} ions of the catalyst.

Cu-Cr catalysts, obtained by sol-gel method in the presence of epoxides, have been investigated in the hydrogenolysis of glycerol to 1,2-propanediol. Structural characterization of the catalysts was performed by means of X-ray diffraction, N_2 physisorption, H_2-temperature programmed reduction, high-resolution X-ray photoelectron spectroscopy, NH_3-temperature programmed desorption, and N_2O titration. Thus, the copper species on the calcined Cu-Cr catalysts and the reduced Cu-Cr catalysts were identified and it was found that there was not a likeness between copper metal surface area and glycerol conversion [4].

Furfural and levulinic acid were hydrogenated to furfuryl alcohol and ã-valerolactone, respectively, using Cu–Cr catalyst, which was synthesized by a modified co-precipitation method. The physical properties of the Cu–Cr catalysts were studied by XRD, EDX, TEM and XPS to reveal their influence on the catalytic performance [5].

The copper chromite spinel nanoparticles ($CuCr_2O_4$) were synthesized via the sol–gel route using citric acid as a complexing agent. The catalysts where characterized by field emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The catalytic activity of the $CuCr_2O_4$ was tested for thermal decomposition of ammonium perchlorate [6].

Mixed oxide materials are used as catalysts used in other processes [7-10]. They are also used in other areas such as different composites [11-14], nanomaterials templated by egg-shell membranes [15], preparation of polyamides composite nanofibres [16], preparation of ceramic and inorganic fibres [17-20], mixed oxide materials for development of integrated gas sensors [21-25], composite type multi-component metal oxide-based sensors [26-28].

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

Experimental part

The precursor complexes were obtained by precipitation at *p*H 7 a mixture of Cu-Cr nitrates in aqueous solution mixed with tartaric acid, 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 IR spectrometry (IR spectometer M-80 Carl Zeiss Jena), XRD (X-ray diffraction apparatus Rigaku last IV), EXAFS (pHi QUANTERA SXM 2010) and TPR.

Thermoprogrammed reduction (TPR) measurements were 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 increasing the temperature in the range 20-500°C. The sample 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 Ar+ 3% H_2 and baseline was stabilized; the system was then heated at 10 $Kmin^{-1}$ 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, IR-spectra (fig. 1) and magnetic measurements led to the following formula for the precursor:

$$[Cr\ Cu_4\ Ta_6] \cdot 5H_2O$$ (where Ta is the tartaric anion).

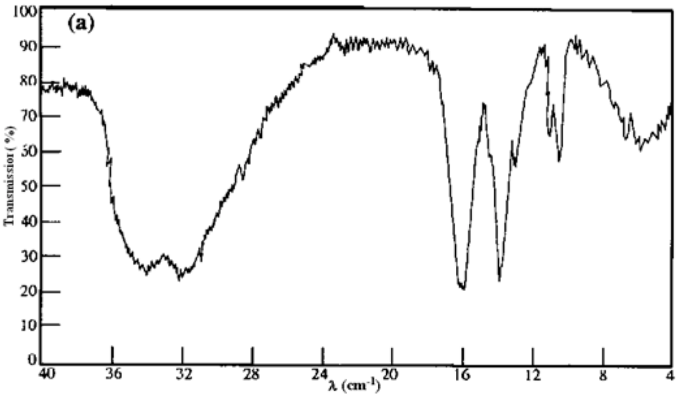

Fig.1.The IR spectra of the 4Cu-1Cr-Ta precursor

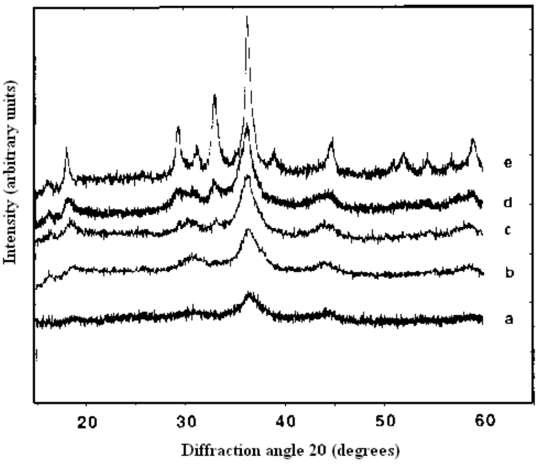

Fig.2.The XRD spectra of the 4Cu-1Cr mixed oxides calcined at different temperatures: a-420°C, b-450°C, c-500°C, d-550°C, e-600°C

Table 1
THE CHARACTERISTICS OF IR SPECTRA OF 4CU:1CR SAMPLE

Sample	$\nu_{(OH)}$ R-OH R-COOH	$\nu_{(OH)}$ H_2O	$\nu_{asimetric}$ (C-O) R-COOH	$\nu_{simetric}$ (C-O) R-COOH	$\delta_{(OH)}$ $\nu_{(C-O)}$	$\gamma_{(OH)}$ $\nu_{(C-C)}$ $\delta_{(OH)}$ R-OH **R-COOH** $\nu_{(CH3)}$	$\nu_{(M-O)}$ $\nu_{asim\,M-O}$ $\nu_{sim\,M-O}$
Cu:Cr:Ta	3475 3100	2940 2850	1628	1375	1120 1062	700 680	590 460

The thermogravimetric stud show that the hydration water of the complex is eliminated up to 200°C.

The decomposition of the complex has two stages:

-first, to corresponds for 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 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 3400-3000 cm^{-1} is typical for stretching vibrations associated HO^- groups (ν_{OH}). The bands at 1620-1580 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 Cu-Cr metallic couple. Sharp and weak bands are found in the region 590-420 cm^{-1} which are attributed to Me-O bonds.

XRD spectra (fig. 2) of calcined samples revealed: at 420°C the mixed oxides 4Cu-1Cr is prevalent amorphous. After increase of calcination temperature, the amount of crystalline lens compounds increases. At 600°C the spinelic stable mixed oxide was identificated: $CuCr_2O_4$, $Cu_2Cr_2O_4$ and small amount of CuO.

With Cu-Cr K-edge EXAFS the local structure of samples calcinated 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).

The x fraction was calculated by relation:

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

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

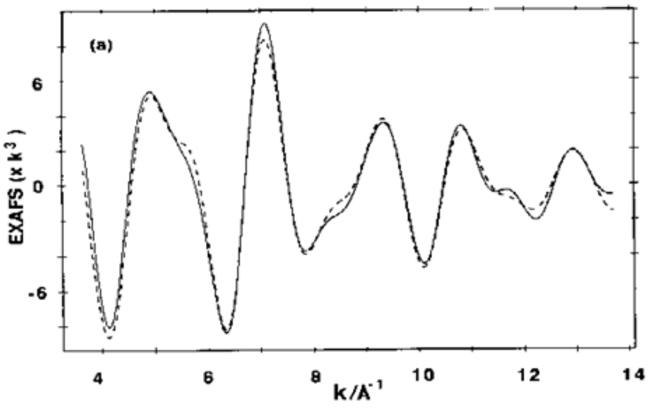

Fig.3 K-edge EXAFS spectra of 4Cu: 1Cr- 420°C sample (amorphous mixed oxides) at K limit of Cr absorbtion: experimental - continuously line; theoretical – discontinuously line

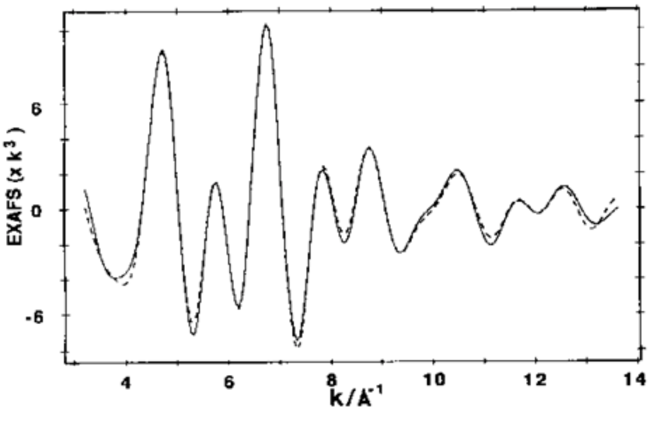

Fig.4. K-edge EXAFS spectra of 4Cu: 1Cr- 600°C sample (spinelic compounds) at K limit of Cu absorbtion: experimental - continuously line; theoretical – discontinuously line

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)
	$CuCr_2O_4 + Cu_2Cr_2O_4$		
Tetrahedral	4	O	1.967
	12	M(6)	3.437
	12	O	3.471
	4	M(4)	3.590
Octahedral	6	O	1.978
	6	M(6)	2.931
	6	M(4)	3.437
	2	O	3.417
	6	O	3.651

Table 3
PARAMETERS OF CRYSTALLINE LENS OF 4CU:1CR MIXED OXIDE SAMPLES

Conditions	Sample	N_1	R_1 (Å)	A_1 $(Å)^2$
At K limit of Cu absorbtion	4Cu:1Cr 420°C	4.1	1.935	0.014
	4Cu:1Cr 600°C	4.5	1.960	0.016
At K limit of Cr absorbtion	4Cu:1Cr 420°C	5.3	1.907	0.010
	4Cu:1Cr 600°C	5.9	1.926	0.011

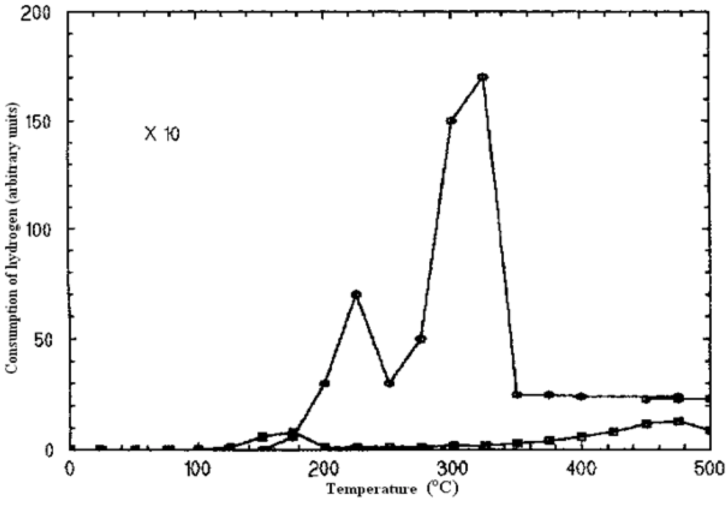

Fig.5. Hydrogen consumption in two reduction cycles for 4Cu:1Cr 600°C: (•) TRP_1, (▪) TRP_2

Figure 5 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 25 times higher than the corresponding consumption in HCR_2; the HCR_1 curve, as well as the HCR_2 curve, exhibits two peaks located at temperatures in the range 180-400°C.

The low temperature peak on the HCR_1 curve can be assigned to the reduction of CuO and the high temperature peak curve is probably due to the transformations $CuCr_2O_4 \rightarrow Cu_2Cr_2O_4$. As shown on the HCR_2 curve, the sample has been restructured, not completely reduced, and, consequently, one still records two forms of hydrogen consumption. The low-temperature form can be assigned either to hydrogen adsorption on metallic copper after the first reduction, or to the reduction of residual forms of CuO.

Conclusions

A mixture of oxides was prepared from complexes of Cu-Cr with tartaric acid. The sample were subsequently submitted to IR spectrometry, XRD, EXAFS and TPR. The TPR curves give information concerning surface reconstruction induced by the interaction of the sample with hydrogen. Calcined at 600°C, Cu-Cr mixed oxides prepared from precursor complexes, have a stable spinelic structure.

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