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Catalytic properties of chromites with a spinel structure in the oxidation of CO and hydrocarbons and reduction of nitrogen oxides

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The catalytic activity of supported chromites $MCr_2O_4/\gamma\text{-}Al_2O_3$ (M = Cu, Co, Mn, Zn, Mg) in the oxidation of CO, C_3H_6, and *o*-xylene and NO_x reduction was studied. The catalytic activity depends on the calcination temperature and cation nature. The features of the formation of the catalysts were studied by the UV-Vis diffuse reflectance and IR spectroscopies.

Key words: catalytic oxidation, reduction, nitrogen oxides, chromites, carbon monoxide, propene, *o*-xylene.

Complex spinel type oxides possess higher activity than simple oxides due to oxygen vacancies on which weakly bound oxygen adsorbs.[1—4] One of such active catalysts is copper chromite $CuCr_2O_4$, which is used for decontamination of exhaust gases from CO.

The goal of this work is to compare the activity of the supported chromites $MCr_2O_4/\gamma\text{-}Al_2O_3$ (M = Cu, Co, Mg, Zn, and Mn) and unsupported chromites in the oxidation of CO, C_3H_6, *o*-xylene and NO_x reduction, *i.e.*, in the underlying reactions for neutralization of the vehicle exhaust gases. The IR and UV-Vis diffuse reflectance spectra were studied to elucidate the features of the catalysts formation.

Experimental

Catalysts were prepared by impregnation of $\gamma\text{-}Al_2O_3$ (IK-02-200) with a solution containing equimolar amounts of $Cr(NO_3)_3$ (chemically pure grade) and nitrates of the corresponding metals (chemically pure grade). After drying for 1 h at 150 °C the samples were heated to 350, 500, or 700 °C. A period of storing at each temperature was 6 h. To prepare bulk spinels, mixtures of the corresponding nitrates were calcined at 350, 500, or 700 °C. The phase composition was estimated by X-ray powder diffraction on a DRON-2 instrument. The spinel structure was revealed by the IR and UV-Vis spectra. Two characteristic bands are known to exist in the 400—700 cm^{-1} frequency range of the IR spectra of spinels,[5] and two characteristic bands are also present in the UV-Vis spectra.[6]

The oxidation of CO and C_3H_6 was carried out on a flow setup at the space velocity of 900 h^{-1}. The volume of the catalyst was 1 cm^3. The reaction mixture contained CO or C_3H_6 (5—6%) and air. The reaction products were analyzed by GC (LKhM-72 gas chromatograph with a thermal conductivity detector, He carrier gas, column length 1 m). The column was packed with 5A molecular sieve to determine CO and with polysorb to determine CO_2.

o-Xylene oxidation was performed in a flow regime on a KL-1 setup (Special Design Office, Institute of Organic Chemistry, Moscow) at the space velocity of 4000 h^{-1}. The hydrocarbon concentration in air was $1 \cdot 10^{-4}$ mol L^{-1}; its content was determined chromatographically according to a procedure described previously.[3]

The reduction of nitrogen oxides was also carried out in a flow setup at the space velocity of 2000 h^{-1} by using a real exhaust gas containing N_2, O_2, CO, CO_2, H_2O, NO_x, and CH_x. The reaction products were analyzed by GC on a Tsvet-100 chromatograph (3 m column packed with polysorb).

The IR spectra were recorded on a Specord M-80 spectrophotometer; the UV-Vis diffuse reflectance spectra were recorded on a Specord M-40 instrument. The specific surface areas of the samples were measured by the BET method with the low-temperature crypton adsorption on a vacuum setup made in the Institute of Physical Chemistry, Russian Academy of Sciences.

Results and Discussion

The formation of the spinel structure was monitored by the IR and UV-Vis spectra. The IR band in the short-wave region is usually attributed to the stretching vibrations of the Cr—O bonds of Cr atoms in the tetragonal environment of O atoms, and the band in the long-wave region is assigned to the vibration of Cr atoms in octahedral environment.[5] Examination of the IR spectra showed that in the case of unsupported chromites (Zn, Co, and Cu), the spinel structure is already formed after calcination at 350 °C. In the case of $MnCr_2O_4$ and $MgCr_2O_4$, higher temperature is required (Table 1). Only spinel bands are present in the spectra of all samples calcined at 500 and 700 °C, indicating their uniphase composition. Figure 1 shows the IR spectrum of $ZnCr_2O_4$ as example. The absorption bands (a.b.) for the sample calcined at 500 °C are narrow and have clear maxima, indicating a slightly imperfect structure. The

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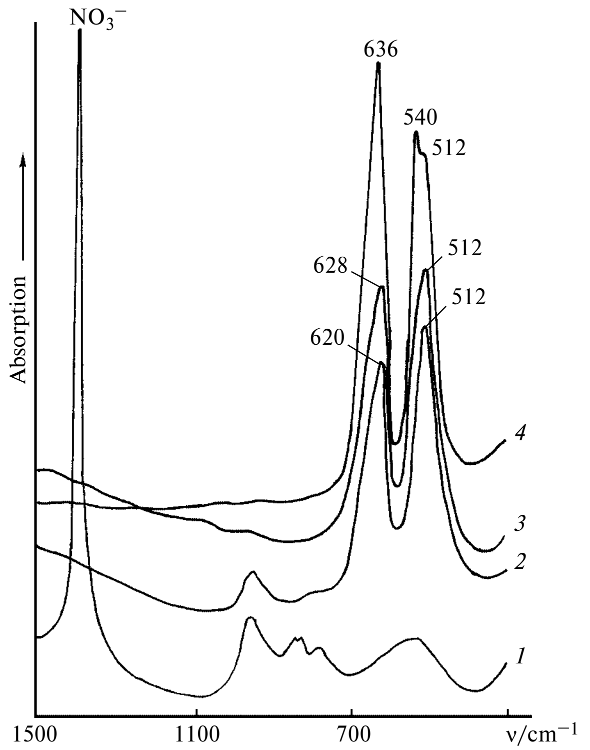

Fig. 1. IR spectra of $ZnCr_2O_4$ calcined at 150 (*1*), 350 (*2*), 500 (*3*) and 700 °C (*4*).

Table 1. Positions of maxima of absorption bands (ν) in the IR spectra of chromites

Chromite	ν*/cm^{-1}		
	A	*B*	*C*
$CoCr_2O_4$	560, 668	556, 636	544, 644
$CuCr_2O_4$	568, 640	520, 616	524, 612
$MnCr_2O_4$	—	572, 628	512, 616
$MgCr_2O_4$	—	556, 660	528, 648
$ZnCr_2O_4$	512, 620	512, 628	540, 636

* The ν values for the samples after calcination at 50 (*A*), 500 (*B*) and 700 °C (*C*) are presented.

splitting of the band 540—512 cm^{-1} in spectrum *4* gives evidence of the lattice deformation after calcination at 700 °C. A small shift of the a.b. maxima to the short-wave region is observed in the spectra of all the chromites studied with increasing calcination temperature (see Table 1). This is likely a consequence of the weakening of the M—O bond, *i.e.*, increasing in the oxygen mobility.

The surface state of the supported chromites was studied by diffuse reflectance spectroscopy. The percentage of the supported chromite was from 1 to 3%. Examination of the diffuse reflectance spectrum for the 1%$MgCr_2O_4$/γ-Al_2O_3 system (Fig. 2) showed that the most fraction of NO_3^- anions is removed at 150 °C. Similar results were obtained for other supported chromites. Two bands, 260—265 and 363—370 nm, are clearly pronounced in the diffuse reflectance spectra of all spinels calcined at 350—700 °C. Comparison with the literature data allows for the assignment of these bands to Cr^{3+} ions in the octahedral coordination.[6—8] Additional bands in the long-wave region at 540, 580, and 625 nm are present in the spectrum of the Co spinel, which can be attributed to cobalt in the octahedral coordination. The appearance of these bands is due to interaction between the cobalt salt and Al_2O_3 to form aluminate $CoAl_2O_4$ (see Refs. 4 and 9). In this case, a $CoCr_2O_4$ and $CoAl_2O_4$ mixture is likely present in the sample.

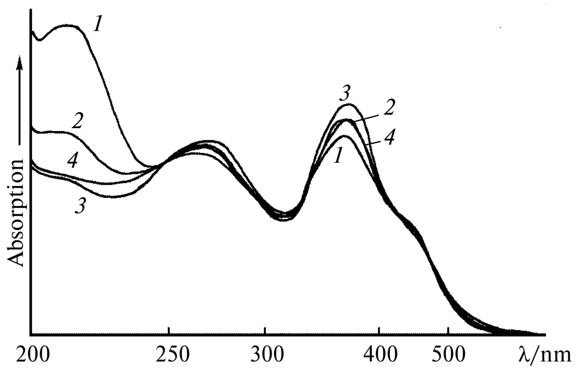

Fig. 2. Diffuse reflectancel spectra of the 1%$MgCr_2O_4$/γ-Al_2O_3 catalyst calcined at 150 (*1*), 350 (*2*), 500 (*3*) and 700 °C (*4*).

A comparison of the IR and diffuse reflectance spectra in UV-Vis regions shows that the formation of the spinel structure on the Al_2O_3 surface is completed at lower temperature than in the bulk catalyst.

All the chromites studied, both bulk and supported, catalyze the oxidation of CO, C_3H_6, and *o*-xylene and the reduction of nitrogen oxides at relatively low temperatures. The temperature at which ~100% conversion is achieved (T_{100}) was accepted as a measure of the catalytic activity of chromites in the oxidation of CO and hydrocarbons.

A comparison of the catalytic and optical properties of the samples allowed for the conclusion that the high catalytic activity is due to the presence of the spinel structure. As can be seen in Table 2, the bulk catalysts are always less active in the oxidation of CO and C_3H_6 than the supported contacts. This is partially due to greater surface areas of the supported catalysts (Table 3) but mainly to the fact that the spinel structure on the carrier surface is formed at lower temperature. This is true for all catalysts except for the cobalt catalyst. Because of diffusion of the Co salt into alumina, cobalt aluminate is formed, which is less active than cobalt chromite (see Table 2). It is the reason for the lower activity of the supported cobalt catalyst compared to the bulk catalyst.

The calcination temperature also affects the performance of chromites. The 100% conversion of CO and C_3H_6 over the catalysts calcined at 350—500 °C, is

Table 2. Catalytic activity of supported and unsupported chromites in the oxidation of CO and C_3H_6

Catalyst	T_{cal}*	T_{100}**	
		CO	C_3H_6
20%$CuCr_2O_4$/γ-Al_2O_3	350	80—90	150
	500	105	160—170
	700	110	170
$CuCr_2O_4$	350	120	160
	500	110	190—200
	700	130	220
20%$CoCr_2O_4$/γ-Al_2O_3	350	150	170
	500	160	200
	700	190	260
$CoCr_2O_4$	350	130	160
	500	140	180
	700	150—160	240
20%$MnCr_2O_4$/γ-Al_2O_3	350	140	150
	500	160	170
	700	210	210
$MnCr_2O_4$	350	190	180
	500	210	170
	700	220	210
20%$ZnCr_2O_4$/γ-Al_2O_3	350	140	180—200
	500	180—190	200
	700	210—220	230—240
$ZnCr_2O_4$	350	180	210
	500	210	240
	700	220	250
20%$MgCr_2O_4$/γ-Al_2O_3	350	190	210
	500	210	180
	700	230	180
$MgCr_2O_4$	350	210	220
	500	220	230
	700	240	240

* Calcination temperature (°C).

** Temperature (°C) at which 100% conversion is achieved.

Table 3. Specific surface areas (S_{sp}) of the supported and unsupported copper chromite

Catalyst	T_{cal}*/°C	S_{sp}/m^2 g^{-1}
$CuCr_2O_4$	350	7.8
20%$CuCr_2O_4$/γ-Al_2O_3	350	32.0
	500	36.0
	700	55.5

* See note* in Table 2.

Table 4. Catalytic activity of chromites supported on γ-Al_2O_3 in *o*-xylene oxidation*

Chromite**	T_{cal}	T_{100}	Chromite**	T_{cal}	T_{100}
	°C			°C	
$CuCr_2O_4$	350	290	$MgCr_2O_4$	350	340
	500	300		500	340
	700	310		700	360
$CoCr_2O_4$	350	335	$ZnCr_2O_4$	350	340
	500	340		500	340
	700	350		700	360
$MnCr_2O_4$	350	315			
	500	310			
	700	330			

* Designations see Table 2.

** Chromite content is 20%.

always achieved at lower temperatures than over chromites calcined at 700 °C. As follows from the examination of the IR spectra, the relatively low activity of chromites is likely due to some deformation of the spinel lattice.

The catalytic behavior of chromites also depends on the cation nature. Bulk chromites can be arranged in the following sequence with respect to decreasing activity in CO oxidation: $CuCr_2O_4$ > $CoCr_2O_4$ > $MnCr_2O_4$ > $ZnCr_2O_4$ > $MgCr_2O_4$. In the case of supported catalysts, this sequence changes as follows : $CuCr_2O_4$ > $MnCr_2O_4$ > $CoCr_2O_4$ > $ZnCr_2O_4$ > $MgCr_2O_4$.

The data on activity of the supported catalysts in *o*-xylene deep oxidation show (Table 4) that the calcination temperature weakly affects this process. However, the highest activity over all the catalysts is achieved at the same calcination temperature, namely, 500 °C. The dependence of the catalytic activity on the cation nature is nearly the same as in the oxidation of CO and C_3H_6: $CuCr_2O_4$ > $MnCr_2O_4$ > $CoCr_2O_4$ > $MgCr_2O_4$ ≈ $ZnCr_2O_4$.

In the reaction products of *o*-xylene oxidation, small amounts of light hydrocarbons (CH_x) and *o*-toluyl acid (TA) were found along with CO_2. Examination of the organic reaction products as a function of the temperature of the run over the $CoCr_2O_4$/γ-Al_2O_3 catalyst (Table 5) shows that when a mixture of xylene vapor with air is passed through the catalyst, a major fraction (60%) of the hydrocarbon adsorbs at already 135—300 °C. As can be seen in Table 5, only small fraction of *o*-xylene (from ~5 to 17%) transforms to TA and light hydocarbons.

Two temperature regions of the reaction can be distinguished: the first from 180 to 280—300 °C and the

Table 5. *o*-Xylene oxidation over catalyst 20%$CoCr_2O_4$/γ-Al_2O_3 calcined at 350 °C

T_{exp} /°C	α*	α′**	Composition of organic products (%)		
	%		CH_x	*o*-Xylene	TA
185	33.6	4.6	0	93.2	6.8
251	68.0	5.8	0	84.6	15.4
282	56.3	7.8	4.1	82.3	14.6
303	34.0	16.8	2.4	76.7	20.9
315	59.8	9.2	0	81.4	18.6
326	76.4	0	Traces	~100	0
340	100	0	0	0	0

* Total conversion.

** *o*-Xylene conversion to TA.

Table 6. Reduction of NO_x to N_2 over chromites supported on γ-Al_2O_3*

Spinel	T_{cal}** /°C	NO_x conversion (%) at various temperatures (°C)				
		150	200	250	300	350
$CuCr_2O_4$	350	38	46	49	51	51
	500	51	56	59	59	59
	700	20	25	29	31	33
$CoCr_2O_4$	350	17	20	23	24	25
	500	20	23	25	28	30
	700	17	18	19	21	20
$MnCr_2O_4$	350	22	37	34	35	—
	500	32	36	39	40	—
	700	20	26	31	45	—
$ZnCr_2O_4$	350	16	16	17	17	17
	500	15	18	20	20	20
	700	12	15	18	20	22
$MgCr_2O_4$	350	18	24	28	28	32
	500	25	33	38	40	41
	700	4	5	7	7	8

* Composition of exhaust gas (%): N_2, 60.9; NO_x, 5.2; CO, 6.8; O_2, 19 (without CH_x and H_2O).

** See note* in Table 2.

second above 300 °C. In the low-temperature region, *o*-xylene slightly undergoes partial oxidation to TA and some deep oxidation along with adsorption. At the temperature of least ~300 °C , deep oxidation prevails. The position of this high-temperature region depends on the spinel nature: for $CuCr_2O_4$, $CoCr_2O_4$, and $MgCr_2O_4$ it begins from 280, 310, and 300 °C, respectively.

To study the reduction of nitrogen oxides to N_2, we used a real exhaust gas containing N_2, O_2, CO, CO_2, NO_x, and CH_x. Oxides NO_x are reduced according to the reaction

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

Several reactions proceed simultaneously, and the most important of them is CO oxidation.[10] The ratio between CO oxidation and NO_x reduction depends on the oxygen concentration. At the oxygen excess, the oxidation of CO and CH_x, proceeds predominantly, and at the small oxygen content, CO is consumed to reduce NO_x. The findings of the runs on NO_x reduction are presented in Table 6. As in oxidation, $CuCr_2O_4$ is most active. The chromites studied can be arranged with respect to their activity in the same sequence as in the oxidation reactions: $CuCr_2O_4 > MnCr_2O_4 > CoCr_2O_4 > MgCr_2O_4 > ZnCr_2O_4$. The calcination temperature slightly affects the catalytic activity. The samples calcined at 500 °C are most active.

Thus, the supported chromites are bifunctional catalysts, which accelerate both the oxidation of hydrocarbons and CO and the reduction of NO_x. As a rule, the catalysts containing Mg^{2+} or Zn^{2+} cations are less active than complex chromites containing cations Mn^{2+}, Co^{2+}, and Cu^{2+}. The oxides containing two transition elements including chromium are more active. The calcination temperatures of 350—500 °C are preferable in the catalyst preparation.

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