Catalytic properties of spinel-type complex oxides in oxidation reactions

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The catalytic activity of $M^IM^{II}_2O_3$ spinel-type complex oxides (M^I = Cu, Ni, Mn, Zn, Mg, Co, M^{II} = Co, Cr, Al) in the oxidation of CO and ethylbenzene has been investigated. The Co-containing catalysts were more active than the Cr- and Al-containing catalysts. The nature of the cation influenced the catalytic activity. Higher activities were observed for the catalysts containing two transition elements. A correlation between the catalytic and adsorption properties was established.

Key words: catalytic oxidation, spinels, carbon monoxide, ethylbenzene, chemisorption.

Complex oxide systems are promising catalysts of oxidation. They are competitive even with catalysts based on platinum metals due to their lower price and rather high activity. Spinel-type complex oxides exhibit high activity in the oxidation of CO and hydrocarbons.[1—4] The activity of spinels is close to the activity of simple oxides, but spinels have the advantage of their stability and the long duration of their activity.

In the present work, a number of groups of spinel-type complex oxides have been synthesized and investigated. The oxidation of CO and ethylbenzene (EB) were used as the model reactions.

Experimental

The catalysts were obtained by calcination of an equimolecular mixture of nitrates at 150 °C for 1 h. Then the temperature was increased to 350—700 °C depending on the composition of the oxide. For the majority of oxides, the calcination temperature was 350 °C. To obtain Mn, Zn, Mg, and Ni chromites, the above-mentioned mixture was heated to 500 °C. In the cases of $CoAl_2O_4$ and $CuAl_2O_4$, the temperature was increased to 700 °C. The catalysts were prepared by a procedure analogous to that described earlier.[5]

The phase compositions were determined by X-ray analysis. The spinel structure of the samples was confirmed by the IR spectra which were recorded on a Specord M-80 spectrophotometer.

The specific surface (S_{sp}) was determined by the BET method using the low-temperature adsorption of krypton. Chemisorption of gases was investigated at 100 °C in a volumetric adsorption apparatus. Prior to measurements, the samples were activated for 6 h at 400 °C at a pressure of 10^{-5} Torr.

The catalytic experiments on the oxidation of CO were performed in a flow-type apparatus. The volume of the catalyst was 1 cm^3. The volume rate was 900 h^{-1}. The reaction mixture contained 5—6 % CO, and the rest was air. The oxidation of ethylbenzene (EB) was performed on a KL-1 instrument under flow conditions. The concentration of hydrocarbon in the air was $1 \cdot 10^{-4}$ mol L^{-1}, and its volume rate was 5500 h^{-1}. The composition of the reaction products was determined by the GC method: CO was analyzed using 5 Å molecular sieves, and polysorb-1 was used for the analysis of CO_2 (helium was the carrier gas).

Results and Discussion

The characteristics of the catalysts obtained are given in Table 1. X-ray analysis and IR spectroscopy showed that the complex oxides synthesized are spinel-type oxides. According to the data reported earlier,[6] spinels have absorption bands at 400—600 cm^{-1} and 600—700 cm^{-1}. The absorption band at 600—700 cm^{-1}

Table 1. Physicochemical properties of the catalysts

Catalyst	S_{sp} /m^2 g^{-1}	ν/cm^{-1}	Temperature of 100 % conversion/°C	
			CO	EB
$CuCo_2O_4$	2.0	568, 660	120	227
$NiCo_2O_4$	5.6	568, 656	120	245
$MnCo_2O_4$	1.6	568, 660	140	235
$ZnCo_2O_4$	2.8	580, 664	160	265
$MgCo_2O_4$	4.8	564, 660	170	250
$CuCr_2O_4$	7.8	576, 628	140	240
$CoCr_2O_4$	14.3	568, 636	160	260
$MnCr_2O_4$	4.2	512, 612	220	280
$ZnCr_2O_4$	1.2	570, 630	220	310
$MgCr_2O_4$	5.8	512, 624	240	305
$NiCr_2O_4$	0.5	512, 612	220	310
$CoAl_2O_4$	30.0	560, 669	180	280
$CuAl_2O_4$	15.4	520, 660	200	380

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belongs to the M—O bond vibrations, and the M cations (Co, Cr, Al) are situated in octahedral coordination. The absorption band at 600 —400 cm^{-1} is due to the M^{I}—O—M^{II} valence vibrations (see Table 1). A number of samples were found to contain minor amounts of simple oxides. The specific surfaces of the investigated oxides were rather similar, *viz.*, 0.5—14.3 $m^2\ g^{-1}$, except for the aluminates, whose S_{sp} was notably higher (15—30 $m^2\ g^{-1}$).

The catalytic activities were compared by using the temperature of 100 % conversion of CO. Figure 1 and Table 1 show that the most active catalysts are the cobaltites: the temperature of 100 % conversion of CO for these compounds varies in the 120—170 °C range; the chromites are next (140—220 °C). The least active catalysts are the aluminates, in the presence of which CO is completely converted at 180—200 °C. The activity of the spinels is influenced to some extent by the nature of the cations. The cobaltites may be put in the following order according to their activities:

$$CuCo_2O_4 > NiCo_2O_4 > MnCo_2O_4 > ZnCo_2O_4 > MgCo_2O_4.$$

An analogous sequence of activities is formed by the chromites (Fig. 2):

$$CuCr_2O_4 > CoCr_2O_4 > MnCr_2O_4 \sim$$
$$\sim ZnCr_2O_4 \sim NiCr_2O_4 > MgCr_4O_4.$$

The low activity of $NiCr_2O_4$ is probably caused by the low S_{sp} of this compound.

Therefore, the presence of two ions of transition elements in catalysts results in an increase in their activity, while the presence of non-transition elements decreases the catalytic activity. These regularities for the changes in activities are also observed in the oxidation of aromatic hydrocarbons. Table 1 shows the temperatures at which the 100 % oxidation of ethylbenzene to form CO_2 and H_2O takes place. Like in the oxidation of CO, the reaction most readily occurs when catalyzed by the cobaltites. The next are the chromites, and the aluminates are the least active catalysts (see Fig. 1). It is interesting that the chromites and aluminates follow the same sequence of changes in activity depending on the nature of the cation, as in the oxidation of CO (see Table 1).

In addition to investigating the catalitic properties, we also studied the chemisorption properties. Table 2 shows that the amounts of CO chemisorbed on the catalysts are larger than those of O_2. Moreover, although the amounts of the chemisorbed gases are different, the chemisorption properties of the different samples have the same regularities as their catalytic properties. The amounts of gases chemisorbed by the cobaltites were the largest. In the case of CO, these amounts varied in the 4.7—1.4 μmol m^{-2} range, and the chemisorption of O_2 amounted to 1.3—0.3 μmol m^{-2}. The corresponding values for chromites are significantly smaller: 2.2—1.1 μmol m^{-2} (CO) and 1.2—0.1 μmol m^{-2} (O_2), while for the aluminates these values are even lower: 1.9—0.1 μmol m^{-2} and 0.3—0.1 μmol m^{-2}, respectively.

Table 2. Chemisorption properties of the catalysts (100 °C)

Catalyst	Amount of chemisorbed gas/μmol m^{-2}	
	CO	O_2
$CuCo_2O_4$	1.39	0.95
$MnCo_2O_4$	2.35	1.35
$ZnCo_2O_4$	1.70	0.65
$MgCo_2O_4$	4.70	0.34
$CuCr_2O_4$	1.80	0.12
$CoCr_2O_4$	1.54	0.10
$ZnCr_2O_4$	1.34	1.16
$MgCr_2O_4$	2.18	0.24
$MnCr_2O_4$	1.08	0.15
$CoAl_2O_4$	0.08	0.07
$CuAl_2O_4$	1.94	0.28

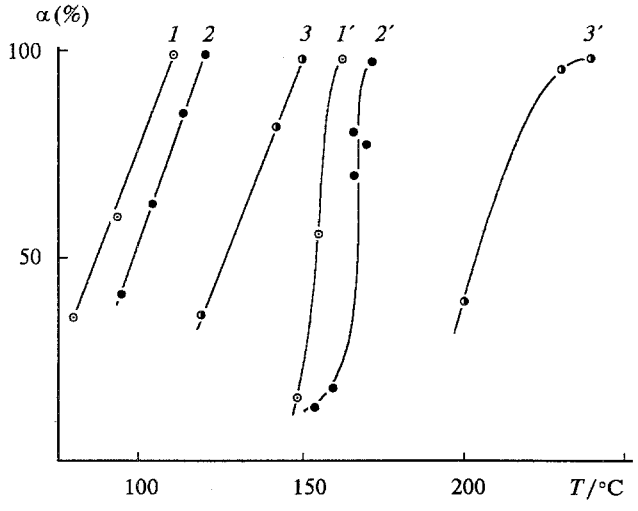

Fig. 1. Dependence of the degree of CO conversion (*1*—*3*) and EB (*1′*—*3′*) on temperature for the catalysts: *1*, $CuCo_2O_4$; *2*, $CuCr_2O_4$; *3*, $CuAl_2O_4$.

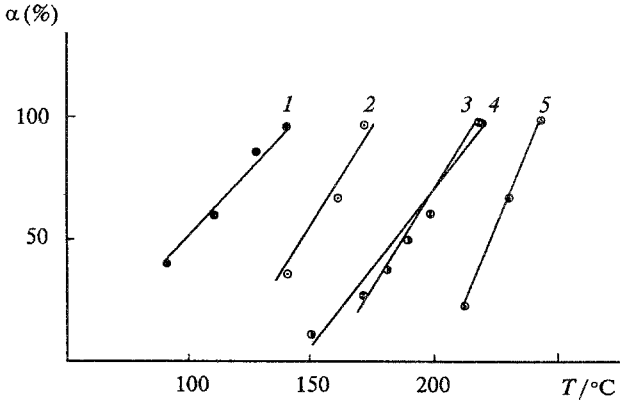

Fig. 2. Dependence of the degree of CO conversion on temperature for the catalysts: *1*, $CuCr_2O_4$; *2*, $CoCr_2O_4$; *3*, $MnCr_2O_4$; *4*, $ZnCr_2O_4$; *5*, $MgCr_2O_4$.

Thus, the worse the adsorptive properties, the lower the catalytic activity. In this connection, a possible mechanism of oxidation may be suggested. Probably, the oxidation reaction catalyzed by any of the investigated samples proceeds not by the "impact" mechanism, which would involve the interaction of the adsorbed oxygen with the CO from the gas phase, but by the Langmuir-Hinshelwood mechanism, *i.e.*, by a reaction between the adsorbed oxygen molecules and the carbon oxide molecules. According to the data reported in Ref. 7, oxygen can form O_2^- and O^- radicals. An adsorbed CO molecule can interact with the oxygen of the catalyst crystal lattice to form a carbonate ion. The presence of ions with the variable valences facilitates these processes, because they provide a source of the electrons necessary for the reduction-oxidation processes. In these processes, the degree of oxidation of the metal changes when it comes into contact with a reactive medium, *i.e.*, oxidation proceeds on a partially reduced catalyst.[8] The conversion of the Co^{3+} ions to Co^{2+} ions proceeds more easily (especially, in the presence of the other transition element ion) than the conversion of Cr^{3+} to Cr^{2+}. Therefore, the activities of Co-containing spinels are higher than those of Cr-containing spinels. In the case of non-transition elements, the number of active centers is smaller, and these spinels are less active.

In the case of ethylbenzene, oxygen-containing compounds are formed on the surface of the catalysts and then decompose to CO_2 and H_2O. The transition element ions favor the formation of the surface compounds,[2] therefore, the regularities in the changes in the catalytic properties of spinels that were observed in the oxidation of CO are also valid for the oxidation of ethylbenzene.

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