Catalytic properties of ferrites in oxidation reactions

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Catalytic activities of ferrites MFe_2O_4 (M = Cu, Co, Ni, Mg, and Zn) and $M^1_{0.5}M^2_{0.5}Fe_2O_4$ (M^1 = Cu; M^2 = Co, Zn, and Mg) in oxidation of CO and ethylbenzene were investigated, and their dependences on the cation nature were established. Higher activities were observed for catalysts containing ions with variable valence (Cu, Co, and Ni). A correlation between catalytic and adsorption properties of ferrites was found.

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

Multicomponent oxide systems are promising catalysts for oxidation, hydrogenation, CO conversion, *etc.* The purpose of this work is to comparatively estimate catalytic activities of ferrites with various cationic compositions in oxidation reactions. Complex oxides with spinel structures of the MFe_2O_4 (M = Co, Cu, Ni, and Zn) and $M^1_{0.5}M^2_{0.5}Fe_2O_4$ (M^1 = Cu; M^2 = Co, Zn, and Mg) types served as catalysts. Reactions of oxidation of CO and ethylbenzene are used as model reactions for estimation of the catalytic activity.

Experimental

The methods for synthesizing the catalysts are similar to those described previously.[1] Two-component oxide catalysts (MFe_2O_4) were prepared by thorough stirring of equimolar amounts of the corresponding nitrates. A mixture was dried for 1 h at 150 °C and then calcinated for 6 h at 500 °C. Three-component ($M^1_{0.5}M^2_{0.5}Fe_2O_4$) and some two-component catalysts were prepared by the carbonate method. A mixture of carbonates was precipitated from a mixture of solutions of the corresponding nitrates. After washing off NO_3^- ions, the precipitates were dried and calcinated for 6 h at 500 °C.

Phase compositions of the catalysts were studied by X-ray diffraction analysis. Structures of oxides obtained were established by IR spectra recorded on a Specord M-80 spectrophotometer. It is known[2,3] that ferrites with spinel structures have absorption bands in the 400—600 cm^{-1} range.

CO was oxidized in a flow-type installation. A reaction mixture contained 5—6 % of CO and 95—94 % of air, the velocity of conveying the mixture was 900 h^{-1}, and the volume of the catalyst was 2 cm^3. Reaction products were analyzed by gas chromatography (a column 1 m long filled with molecular sieves (5 Å) for determining CO and Polysorb for determining CO_2, He was used as carrier gas, and a katharometer served as a detector).

Hydrocarbons were oxidized using a standard KL-1 installation in a flow-type reactor. The concentration of ethylbenzene was $1 \cdot 10^{-4}$ mol L^{-1}, the velocity of conveying a vapor-air mixture was 6000 h^{-1}, and the weight of catalyst was ~1.0 g. The reaction was followed by a decrease in the concentration of ethylbenzene, which corresponded to an increase in the concentration of CO_2. The concentration of ethylbenzene was determined by chromatography (a column of 2000×3 mm filled with tricresyl phosphate on Celite-545, a flame-ionization detector, 90 °C).

The specific surface was measured by the BET method from the low-temperature adsorption of Kr. Chemisorption of CO and O_2 was studied in a volume adsorption setup at 100 °C. Before measurements samples were kept for 6 h at 10^{-5} Torr.

Results and Discussion

The main parameters of the catalysts obtained are presented in Tables 1 and 2. The data of X-ray diffraction analysis and the IR spectra show that the samples synthesized are spinels. The values of the cell parameters almost coincide with those presented in the literature.[3] Insignificant amounts of simple oxides are present in all samples. An increase in the temperature of synthesis results, as a rule, in a decrease in the content of admixtures.

The IR spectra of the catalysts contain absorption bands within the 400—600 cm^{-1} range typical of ferrites with spinel structures. The IR spectrum of $CoFe_2O_4$ is presented in Fig. 1 as an example. Two intense bands at 584 and 392 cm^{-1} are assigned to the spinel structure. A small peak at 480 cm^{-1} is related to the admixture of Fe_2O_3. The bands related to the spinel structure are underlined in Table 1. The IR spectra of three-component oxides exhibit the bands characteristic of simple and two-component oxides. The spectra of $Cu_{0.5}Co_{0.5}Fe_2O_4$ and $Cu_{0.5}Zn_{0.5}Fe_2O_4$ exhibit a band at 460 cm^{-1} and a broad band with a maximum at 584 cm^{-1}, which is probably the result of overlapping of several bands. The IR spectrum of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ contains two bands typical of the spinel structure (568

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Table 1. Physicochemical properties of catalysts

Composition	S_{sp} /m^2 g^{-1}	Cell parameter /Å	IR, ν/cm^{-1}	Admixtures	Q/μmol m^{-2} (100 °C)		T/°C (α = 100 %)*	
					CO	O_2	CO	Ethylbenzene
$CuFe_2O_4$	6.0	8.44	556, 484, 460, 340	CuO, Fe_2O_3	14.5	2.7	150	255
$CoFe_2O_4$	2.0	8.40	584, 480, 392	Fe_2O_3	2.4	2.7	210	300
$NiFe_2O_4$	4.0	8.34	596, 480, 408	Fe_2O_3	3.0	1.9	290	325
$MgFe_2O_4$	2.0	8.35	580, 448, 360		1.4	0.8	310	350
$ZnFe_2O_4$	4.0	8.43	548, 436, 336	ZnO, Fe_2O_3	1.4	0.9	330	335

* The temperature of the 100 % conversion.

Table 2. Properties of three-component oxides

Catalysts	S_{sp} /m^2 g^{-1}	IR, ν/cm^{-1}	T/°C (α = 100 %)	
			CO	Ethylbenzene
$Cu_{0.5}Co_{0.5}Fe_2O_4$	18.0	584,460	110	265
$Cu_{0.5}Zn_{0.5}Fe_2O_4$	10.0	584,460	190	305
$Cu_{0.5}Mg_{0.5}Fe_2O_4$	7.0	568,476	280	315

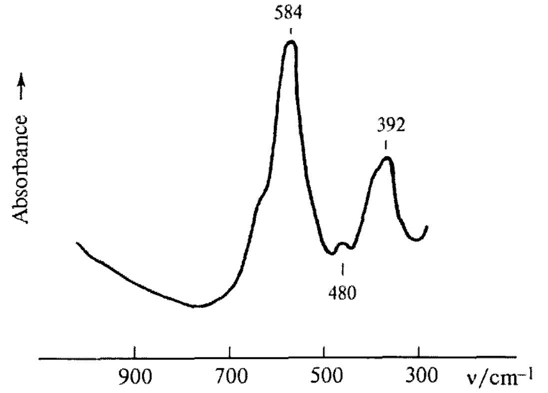

Fig. 1. IR spectrum of $CoFe_2O_4$.

and 476 cm^{-1}). The spectral data for simple oxides are presented in Table 3. It is seen that the positions of the bands corresponding to simple and complex oxides differ noticeably.

Table 3. Properties of simple oxides

Oxide	IR, ν/cm^{-1}	T/°C	α (% of CO)
CuO	520,580	200	100
Fe_2O_3	337,384,480,564	270	100
ZnO	440,500,540	360	60
MgO	504,516	350	80

The temperature of the 100 % conversion of a substance was used for the estimation of the catalytic activity. The comparison of the results on CO oxidation showed that reactions involving simple oxides occur at higher temperatures than in the presence of spinels (see Tables 1 and 3). However, the activities of spinels of different compositions also differ strongly (Figs. 2 and 3). The analysis of the data obtained allowed one to draw a conclusion that the activity of ferrites toward oxidation of both CO and ethylbenzene depends on the cation nature. The activities of the catalysts (for CO oxidation) decrease in the following series: $CuFe_2O_4 > CoFe_2O_4 > NiFe_2O_4 > MgFe_2O_4 > ZnFe_2O_4$. The difference in the activities of the samples cannot be explained by their different specific surfaces. This is evidenced by the experiments with $CoFe_2O_4$ and $CuFe_2O_4$ obtained by two methods. The specific surface of $CoFe_2O_4$ synthesized by the carbonate method was ~18 m^2 g^{-1}, while the specific surface of that prepared from nitrates was ~2 m^2 g^{-1}. However, CO was completely oxidized on both samples at close temperatures

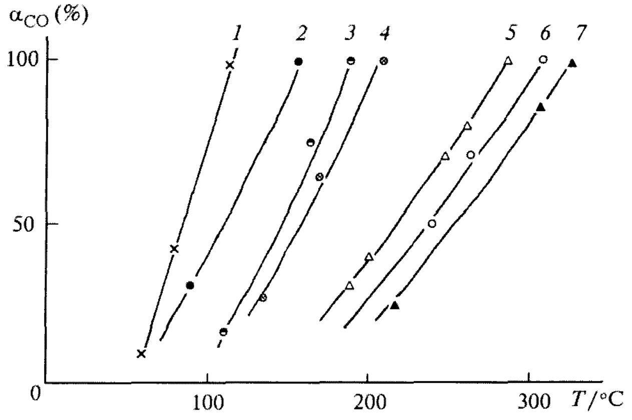

Fig. 2. Temperature dependence of the degree of CO conversion with catalysts of various compositions: *1*, $Cu_{0.5}Co_{0.5}Fe_2O_4$; *2*, $CuFe_2O_4$; *3*, $Cu_{0.5}Zn_{0.5}Fe_2O_4$; *4*, $CoFe_2O_4$; *5*, $NiFe_2O_4$; *6*, $MgFe_2O_4$; *7*, $ZnFe_2O_4$.

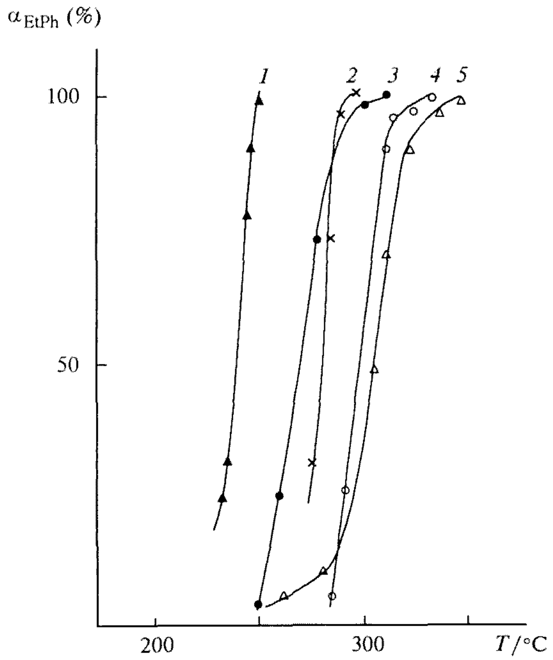

Fig. 3. Temperature dependence of the degree of conversion of ethylbenzene with catalysts of various compositions: *1*, $CuFe_2O_4$; *2*, $CoFe_2O_4$; *3*, $NiFe_2O_4$; *4*, $ZnFe_2O_4$; *5*, $MgFe_2O_4$

(200 and 210 °C, respectively). The same was observed in the case of $CuFe_2O_4$. The specific surface of the sample obtained by the carbonate method was ~23 m^2 g^{-1}, while that of the sample prepared from nitrates was 6 m^2 g^{-1}. The differences in catalytic activity were small: the temperatures of the complete CO oxidation were 130 and 150 °C, respectively.

The activity of ferrites in the oxidation of ethylbenzene also depends on the cation nature, and the regularity of its change is almost the same as for CO oxidation. A small difference was observed in behaviors of $ZnFe_2O_4$ and $MgFe_2O_4$. One can draw a conclusion from the data obtained that ferrites containing metal cations with variable valence are more active. This conclusion is confirmed by the experiments with three-component catalysts (see Fig. 2). The complete oxidation of CO in the presence of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ is observed at 190 °C, and ethylbenzene is completely oxidized at 305 °C, *i.e.*, the activity of this catalyst is higher than that of $ZnFe_2O_4$ but lower than the activity of $CuFe_2O_4$. $Cu_{0.5}Mg_{0.5}Fe_2O_4$ occupies the same intermediate position in the oxidation of CO and ethylbenzene. It is likely that the main contribution to the activity of such catalysts is made by Cu ions. Spinel containing two cations with variable valence, $Cu_{0.5}Co_{0.5}Fe_2O_4$, is more active. In the presence of this catalyst, the 100 % conversion of CO occurs at the lowest temperature (~110 °C). The activities of $CuFe_2O_4$ and $Cu_{0.5}Co_{0.5}Fe_2O_4$ are close in the oxidation of ethylbenzene.

Adsorption properties of ferrites were studied along with catalytic properties. It is seen from the data presented in Table 1 that the values of chemisorption of CO are insignificantly greater than those of chemisorption of O_2 nearly for all samples. The correlation between catalytic and adsorption properties is rather distinct: the higher chemisorption of gases on ferrites, the higher their activity in oxidation of CO and ethylbenzene. These results allow one to conclude that the oxidation on ferrites occurs according to not "impact" mechanism, which supposes the reaction between chemisorbed oxygen and CO molecules from the gaseous phases. The Langmuir—Hinshelwood mechanism is more probable, according to which the reaction occurs between adsorbed molecules of oxygen and CO.

There are many hypotheses about the mechanism of oxidation of CO and hydrocarbons.[4–6] The majority of authors believe that O_2^- and O^- radicals, which react with CO or hydrocarbon, are formed on the surface. The formation of carbonate ions (in the case of CO) and active hydrocarbon complexes is possible at intermediate stages of the process. The reduction and reoxidation of the catalytic surface accompanied by change in valence of ions can occur during the oxidation. The difference in activities of the catalysts studied is related to the degree of participation of a cation in these processes. Therefore, the catalysts containing easily reducible Cu, Co, and Ni ions exhibit higher activities than oxides containing Mg^{2+} or Zn^{2+} ions. Higher activities of spinels compared to those of simple oxides are related to specific features of their structures. Spinel has two sublattices, tetrahedral and octahedral. Some cavities in these sublattices are not occupied by cations. This structure can be easily rearranged, which results in electron transfer by adsorbed oxygen molecules to form oxygen radical ions that react with adsorbed molecules of CO or hydrocarbon.

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