Catalytic properties of manganites in the oxidation of CO and hydrocarbons

G. N. Pirogova,* N. M. Panich, R. I. Korosteleva, and Yu. V. Voronin

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: 007 (095) 952 7514

Manganites with a spinel structure MMn_2O_4 (M = Co, Cu, Zn, Mg) and $M^1_{0.5}M^2_{0.5}Mn_2O_4$ (M = Co, Cu, Zn, Mg) have been synthesized and tested in the catalytic oxidation of CO, C_3H_6, and ethylbenzene. The dependence of the catalytic activity of the manganites on the nature of the cation has been established. The spinels containing transition metal ions (Cu, Co) are more active. A relation between catalytic and adsorption properties of manganites has been established. The participation of the lattice oxygen in the oxidation of CO to CO_2 has been found. The mechanism of the oxidation is discussed.

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

Complex oxides with a spinel structure are promising catalysts for deep oxidation of hydrocarbons and CO.[1] Among known spinels, manganites are less studied, although some authors have shown their high activity and stability in oxidative reactions.[2,3]

The goal of this work is to compare the catalytic activity of manganites of various cationic compositions in the oxidation of CO, propene, and ethylbenzene.

Experimental

The procedures for the synthesis of manganites are similar to those described earlier.[4] Two-component oxides of the MMn_2O_4 (M = Cu, Co, Zn, Mg) type were obtained by two methods, *viz.*, by the calcination of a mixture of nitrates and by a carbonate method. In the first case, a mixture of salts was heated for 1 h at 150 °C and then for 6 h at 500 °C. In the second case, an aqueous solution of a mixture of nitrates was treated with sodium carbonate, NO_3^- was washed off the obtained precipitate, which was then dried and calcined at 500 °C. Three-component oxides of the $M^1_{0.5}M^2_{0.5}Mn_2O_4$ (M = Co, Cu, Zn, Mg) type were obtained by the carbonate method. The oxides were identified by X-ray diffraction (XRD) and IR spectroscopy. The spinel structure is known to be characterized by two typical bands in the 400—700 cm^{-1} region.[5,6] The IR spectra were registered on a Specord M-80 spectrophotometer.

Catalytic oxidation of CO and C_3H_6 was carried out on a flow setup. A reaction mixture contained 5—6% CO (or C_3H_6) and 94—95% air; the volume of a catalyst was 2 cm^3. The reaction products were analyzed by gas chromatography (GC) on a Tsvet-100 chromatograph (thermal conductivity detector, carrier-gas He, a column of 1 m in length packed with a 5 Å molecular sieve for the determination of CO and a column with Polysorb for the determination of CO_2).

The catalytic activity of the samples was also studied in a pulse regime. The starting mixture (CO—air or CO—N_2) contained ~20% CO. During the reaction, a pulse of a substance (0.65 mL) in a He flow (~40 mL min^{-1}) was passed through a catalyst. The products were analyzed by GC.

The oxidation of ethylbenzene was studied on a KL-1 installation with a flow reactor. The experimental conditions have been described previously.[7] A mixture of ethylbenzene vapor and air was passed through a catalyst; and the reaction was monitored by the loss of ethylbenzene to which a simultaneous increase in the CO_2 concentration corresponded.

The temperature of 100% conversion was used for a comparison of the catalytic activity.

The specific surface area was measured by the Brunauer—Emmett—Teller (BET) method with the use of the low-temperature adsorption of krypton. The chemisorption of CO and O_2 was studied on a volumetric adsorption installation at 100 °C. Before measurements, the substances were trained at 10^{-5} Torr for 6 h.

Results and Discussion

Characteristics of the catalysts studied are presented in Tables 1—3. According to the data of XRD and IR spectroscopy, the oxides obtained have a spinel structure AB_2O_4. Two absorption bands that are related to the stretching vibrations of the metal—oxygen bonds were observed in the 400—700 cm^{-1} region. The short-wave band has been assigned to the vibrations of the metal atoms (A) in the tetrahedral environment of oxygen atoms (*i.e.*, M—O), and the long-wave band has been assigned to the vibration of the metal atoms (B) in the octahedral caves of a spinel (Mn—O).[5] The differences in the positions of the bands in the IR spectra of different samples are due to the influence of admixtures, simple oxides, and to the mutual influence of the metals occurring in the tetrahedral and octahedral sublattices. As the calcination temperature increases, the amount of

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Table 1. Characteristics of the catalysts obtained from nitrates

Catalyst	T_{ox}/°C	S_{sp} /m^2 g^{-1}	a/Å	Admixtures	Q/μmol m^{-2}		IR spectrum, ν/cm^{-1}	T_α/°C (α = 100 %)		
					CO	O_2		CO	EB	C_3H_6
$CoMn_2O_4$	350	1.2	8.13	Mn_2O_3, CoO	21.0	1.51	572, 660	90	240	250
$CuMn_2O_4$	700	2.2	8.29	CuO, MnO_2	2.0	0.61	512, 630	100	250	280
$ZnMn_2O_4$	350	7.2	8.12	Mn_2O_3, ZnO	0.7	0.24	520, 624	170	270	360
$MgMn_2O_4$	350	1.0	8.08	MgO	2.0	0.30	524, 610	220	285	350

Note: T_{ox} is the temperature of the calcination of oxides; T_α is the temperature of 100% conversion; a is a parameter of a lattice; Q is the amount of chemisorbed gas at 100 °C, EB is ethylbenzene.

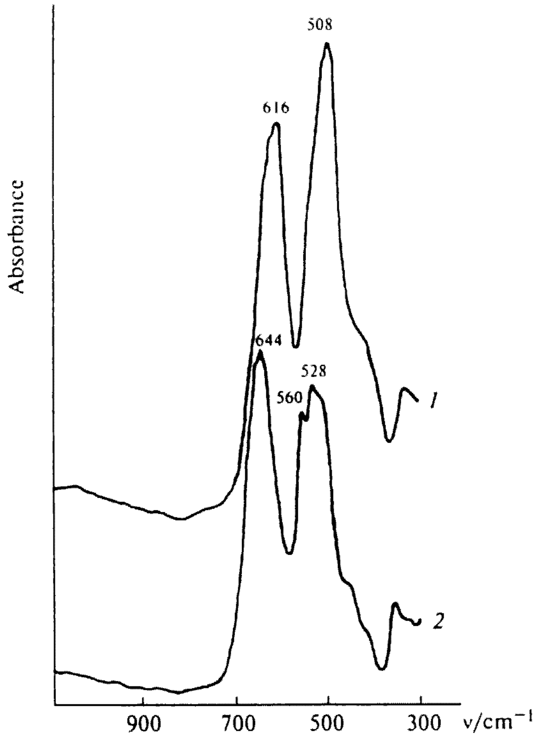

Fig. 1. The IR spectra of spinels: *1*, $Cu_{0.5}Zn_{0.5}Mn_2O_4$, *2*, $Co_{0.5}Mg_{0.5}Mn_2O_4$.

admixtures decreases; hence, the intensities of the bands in the IR spectrum related to the spinel structure increase and the bands of the simple oxides disappear.

In the case of some three-component oxides, three bands in the 400—700 cm^{-1} region were observed that seems to be due to the presence of two cations in the tetrahedral caves. Fig. 1 shows two types of spectra of three-component oxides.

As can be seen in Tables 1 and 2, the preparation method affects the specific surface area and catalytic activity of manganites. In all three reactions studied, the temperature of complete conversion is lower for the catalysts prepared by the carbonate method. Apparently, one of the reasons for this is their higher specific surface area. The cation nature significantly affects the activity of manganites. The oxidation of all substances studied occurs most efficiently over $CoMn_2O_4$, followed by $CuMn_2O_4$. $ZnMn_2O_4$ and $MgMn_2O_4$ are less active. Thus, the presence of two cations of alternating valency enhances the activity of the catalysts. Similar data have been obtained previously for other complex oxides: chromites and cobaltites.[7]

Table 2. Characteristics of the catalysts obtained by the carbonate method

Catalyst	S_{sp}/m^2 g^{-1}	T_α/°C (α = 100 %)		
		CO	EB	C_3H_6
$CoMn_2O_4$	12.4	100	215	240—250
$CuMn_2O_4$	10.0	100	195	230—250
$ZnMn_2O_4$	14.0	130	210	260—270
$MgMn_2O_4$	2.5	130	225	280—290

The activity of three-component oxides is intermediate between those of corresponding two-component oxides (Fig. 2, Table 3). Let us consider some examples. Complete oxidation of CO and ethylbenzene over $CoMn_2O_4$ is achieved at 100 and 215 °C, respectively, while that over $MgMn_2O_4$ is achieved already at 130 and

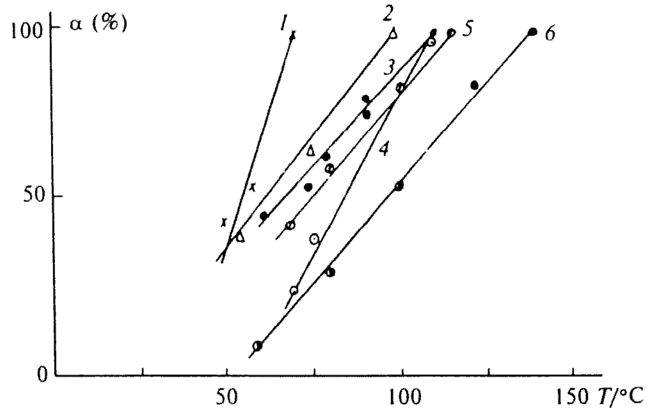

Fig. 2. CO conversion over the catalysts: *1*, $Cu_{0.5}Co_{0.5}Mn_2O_4$, *2*, $Cu_{0.5}Mg_{0.5}Mn_2O_4$, *3*, $Co_{0.5}Zn_{0.5}Mn_2O_4$, *4*, $Cu_{0.5}Zn_{0.5}Mn_2O_4$, *5*, $Co_{0.5}Mg_{0.5}Mn_2O_4$, *6*, $Mg_{0.5}Zn_{0.5}Mn_2O_4$.

Table 3. Properties of three-component oxides

Catalyst	S_{sp}/ m^2 g^{-1}	IR spectrum, ν/cm^{-1}	T_α/°C (α = 100 %)		
			CO	EB	C_3H_6
$Cu_{0.5}Co_{0.5}Mn_2O_4$	10.6	524, 612	70	195	250
$Cu_{0.5}Zn_{0.5}Mn_2O_4$	9.0	508, 616	110	195	300
$Cu_{0.5}Mg_{0.5}Mn_2O_4$	8.2	476, 520, 552, 600	100	210	310
$Co_{0.5}Mg_{0.5}Mn_2O_4$	8.0	528, 560, 644	115	220	270
$Co_{0.5}Zn_{0.5}Mn_2O_4$	2.4	532, 552, 644	110	215	240
$Mg_{0.5}Zn_{0.5}Mn_2O_4$	6.6	432, 532, 552, 644	140	225	330

225 °C. The CO oxidation on the $Co_{0.5}Mg_{0.5}Mn_2O_4$ catalyst ceases at 115 °C and that of ethylbenzene ceases at 220 °C.

As a whole, the oxidation of CO and ethylbenzene over all three-component catalysts occurs at moderate temperatures when there are two transition metals in the oxide. The oxidation of propene requires higher temperatures than in the case of two-component catalysts (Fig. 3).

Chemisorption properties were studied simultaneously with the catalytic properties. The chemisorption of CO and O_2 was investigated at 100 °C. As can be seen in Table 1, the amount of chemisorbed CO is higher than that of O_2. More catalytically active samples chemisorb more gases. The exception to the general rule toward CO is $MgMn_2O_4$. As a whole, one can conclude that the higher the adsorption capacity, the higher the catalytic activity.

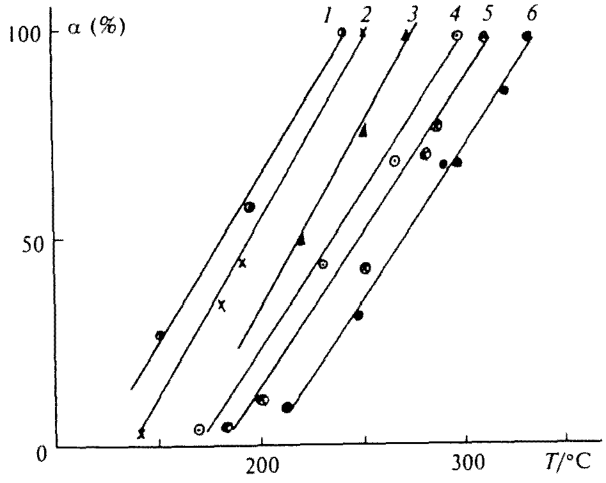

Fig. 3. C_3H_6 conversion over the catalysts: *1*, $Co_{0.5}Zn_{0.5}Mn_2O_4$, *2*, $Cu_{0.5}Co_{0.5}Mn_2O_4$, *3*, $Co_{0.5}Mg_{0.5}Mn_2O_4$, *4*, $Cu_{0.5}Zn_{0.5}Mn_2O_4$, *5*, $Cu_{0.5}Mg_{0.5}Mn_2O_4$, *6*, $Mg_{0.5}Zn_{0.5}Mn_2O_4$.

The correlation between the catalytic and chemisorption properties indicates that CO oxidation does not proceed *via* an "impact" mechanism that assumes the interaction of adsorbed oxygen with CO from the gas phase. A so-called concerted mechanism, in which adsorbed molecules of CO and oxygen react with each other, is more probable. The high activity of the catalysts containing transition metal ions is connected with their ability to transfer electrons to the adsorbed oxygen molecules to form the radical ions $O_2^{\cdot -}$ and $O^{\cdot -}$ that participate in catalysis.

It is known[1] that under the conditions of catalytic oxidation, the concentrations of oxygen at the surface and in the bulk can differ from the equilibrium values, and consequently the probability of

$$O^-_{ads} \rightleftharpoons O^{2-}_{lattice},$$

transitions increases, *i.e.*, the transition of the lattice oxygen onto a surface (to an adsorbed state) is possible. We carried out the CO oxidation in a pulse regime using $CuMn_2O_4$ as an example and found the participation in the reaction of the oxygen of the surface layer. As a result of the interaction of the CO pulse with the surface of $CuMn_2O_4$ at ~70 °C, CO_2 was observed in the reaction products, and its content increased as the reaction temperature increased. The reaction stoichiometry corresponds to the oxidation of CO to CO_2, and complete oxidation is achieved at 250 °C (Fig. 4). Fig. 4 presents the data concerning the first pulse: when the number of pulses (*n*) increases, the CO conversion (α) drops, especially at low temperatures. As the reaction temperature increases, the dependence of α on *n* becomes weakly noticeable. Similar phenomena were observed when the CO pulse was diluted with an inert gas (N_2). The observed dependence on *n* indicates that the process occurs with the participation of the lattice oxygen, and

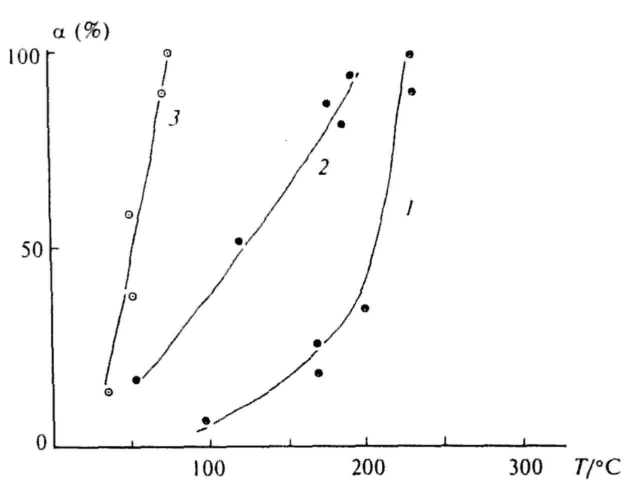

Fig. 4. CO conversion over $CuMn_2O_4$ in a pulse regime at various compositions of the starting mixture: *1*, CO, *2*, CO + N_2, *3*, CO + air.

the stage of oxygen diffusion from the bulk to the surface is the rate-determining stage. The introduction of oxygen into a pulse (CO—air) results in some increase in the CO conversion; the dependence on *n* is not obviously expressed. Apparently, in this case, the reactive oxygen comes from the gas phase. Thus, one can suggest that under the conditions of high-temperature catalytic oxidation, migration of oxygen to the surface is possible and, in the opinion of the authors of Ref. 1, can be an accompanying stage of the process.

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