Oxidation of CO and hydrocarbons over perovskite-type complex oxides

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The catalytic activity of perovskites $M^IM^{II}O_3$ (M^I = La; M^{II} = Co, Mn, Cr, Al, Ni, and V) and M^ICoO_3 (M = Y, Nd, Sm, and Er) in the oxidation of CO, propylene, and ethylbenzene was investigated. The highest activity was observed for the M^ICoO_3 catalysts with perfect perovskite structure. The nature of the rare-earth element has no influence on the catalytic activity. Deformation of the octahedral coordination of the metal was found for the less active catalysts. The interaction of gases (CO, CO+air) with the catalyst surface was investigated. The more active catalysts adsorb a greater amount of O_2, and the adsorption occurs in the temperature region of the oxidation reaction. The activities of the perovskite- and spinel-type catalysts were compared under similar conditions.

Key words: perovskites, spinel, carbon monoxide, propylene, ethylbenzene, catalytic oxidation.

Complex oxides with perovskite-like structure are promising catalysts for several processes, including oxidation reactions.[1—3] Perovskites possess higher activity and stability as compared to simple oxides.[4]

The purpose of this work is to study the activity of perovskites in the oxidation of CO, C_3H_6, and ethylbenzene (EB). Perovskites $M^IM^{II}O_3$ (M^I = La; M^{II} = Co, Mn, Cr, Al, Ni, and V) and M^ICoO_3 (M^I = Y, Nd, Sm, and Er) were used as the catalysts.

Experimental

Catalysts were obtained by the known method.[5] Metal nitrates were dissolved in a minimum amount of water, and oxalic acid was added to the solution to precipitate the oxalate complex $La[M(C_2O_4)_3]$, which was dried and calcined for 6 h at 500 or 700 °C.

Catalysts were studied by IR spectroscopy. The perovskite structure exhibits two characteristic bands in the 400—700 cm^{-1} region. IR spectra were recorded on a Specord M-80 spectrophotometer.

The specific surface was determined by the BET method from the low-temperature adsorption of Kr.

Oxidation of CO and C_3H_6 was carried out in a flow setup with a flow rate of 900 h^{-1}. The starting gas mixture contained 5—6% of the oxidized gas and 94—95% air. The catalyst volume was 1 cm^3.

The reaction products were analyzed by GLC (a thermal conductivity detector, He as the carrier gas). A column with molecular sieves 5A (T = 30 °C) was used for the determination of CO, and a column packed with Polysorb (T = 70 °C) was used for the determination of CO_2.

EB was oxidized in a flow reactor on a KL-1 installation (Designing Bureau of the Institute of Organic Chemistry, RAS, Moscow). The concentration of EB vapor in air was 0.1 mol m^{-3}. The conditions of analysis have previously been described.[6]

The interaction of gases with the catalyst surface was studied by the pulse method on a KL-1 installation using 1.5 g of the catalyst. The starting gas mixture contained 14—18 mol.% CO; the rest was air or N_2. The pulse volume was 0.65 mL. The gas mixture was passed through the catalyst bed in a He flow at temperatures from −20 °C to 300—400 °C. The composition of gases was examined by GC.[6]

The activities of the catalysts were compared by the temperature corresponding to a 50% or 100% conversion of the starting reagents (α).

Results and Discussion

The study of the IR spectra of samples showed that carbonate groups are retained in their structure at the calcination temperature of 350—500 °C. The bands corresponding to these groups disappear at 700 °C, and the bands in the 400—700 cm^{-1} region characteristic of perovskites show up more distinctly. The high-frequency band is usually ascribed to vibrations of the M—O bond of the metal in the octahedral coordination.[7] The low-frequency band is attributed to vibrations of the valence M^I—O—M^{II} bonds. Pronounced narrow bands were observed in the IR spectra of the $MCoO_3$ compounds (M is a rare-earth element (REE)). More diffuse broad bands appeared in the spectra of $LaAlO_3$, $LaNiO_3$, and $LaVO_3$, which indicates deformation of the octahedral environment of the metal.

The activity of the perovskites studied depends on the temperature of their calcination (Tables 1 and 2, Figs. 1 and 2). The most active samples were mainly

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Table 1. Influence of the composition of the $MCoO_3$ catalysts (M is REE) and calcination temperature (T_{exp}) on their properties

Catalyst	T_{exp} /°C	S /$m^2 g^{-1}$	ν /cm^{-1}	T_c/°C CO	Ethylbenzene	C_3H_6*
$YCoO_3$	350	11.7	576, 664	90	—	—
	500	5.6	576, 668	100	250	250
	700	7.0	572, 664	100	—	—
$LaCoO_3$	350	12.6	—	120	—	—
	500	5.4	580, 668	120	240	270
	700	10.0	576, 664	180	—	—
$SmCoO_3$	350	2.9	—	180	—	—
	500	11.0	580, 664	140	265	330
	700	16.5	576, 664	155	—	—
$NdCoO_3$	350	13.1	576, 660	80	—	—
	500	9.9	572, 664	90	245—255	260
	700	3.5	572, 664	90	—	—

Note. The following designations were used: S is the specific surface, ν is the frequency of the band in the IR spectrum, and T_c is the temperature of overall conversion. * α = 50%.

Table 2. Influence of the composition of the $LaMO_3$ catalysts and calcination temperature (T_{exp}) on their properties

Catalyst	T_{exp} /°C	S /$m^2 g^{-1}$	ν /cm^{-1}	T_c/°C CO	Ethylbenzene	C_3H_6*
$LaMnO_3$	350	10.4	—	170	—	—
	500	8.8	400, 530	130	265	350
	700	7.5	400, 612	140	—	—
$LaNiO_3$	350	—	—	210	—	—
	500	9.7	400	210	290	310
	700	10.4	440, 640	180	—	—
$LaCrO_3$	350	7.9	—	230	—	—
	500	5.4	416, 608	260	310	320
	700	3.6	416, 608, 636	260	—	—
$LaVO_3$	350	7.5	440	230	—	—
	500	8.9	440, 616	230	330	470
$LaAlO_3$	700	7.0	440, 676	280	365	370

Note. For designations, see Table 1. * α = 50%.

obtained after thermal treatment at 500 °C; therefore, the activities were compared for these catalysts, except for $LaAlO_3$, whose synthesis requires a higher temperature of treatment (see Table 2).

The oxidation of CO occurs most easily on the cobalt-containing catalysts (see Table 1, Fig. 1). The activities of the samples containing rare-earth elements as the M^I cation are almost equal. The $LaMnO_3$ sample is close in activity to these samples. The low activity of $LaNiO_3$, $LaVO_3$, and $LaAlO_3$ is most likely explained by the poorly formed perovskite structure.

Almost the same tendency is retained for the oxidation of EB (see Tables 1 and 2, Fig. 1). However, in this case, the temperature of complete combustion is 100—150 °C higher than that for CO.

The temperature dependence of the degree of conversion of C_3H_6 (see Fig. 2) differs noticeably from the data on CO oxidation (see Fig. 1). In the first case, the reaction proceeds at higher temperatures. In addition, C_3H_6 is characterized by a smaller slope of the temperature curves (see Fig. 2).

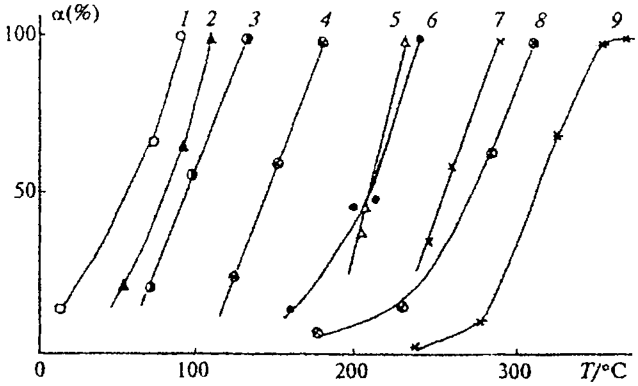

Fig. 1. Temperature effect on the conversion of CO (α) (*1—5*) and ethylbenzene (*6—9*) on different catalysts: *1*, $NdCoO_3$; *2*, $YCoO_3$; *3*, $LaMnO_3$; *4*, $LaCrO_3$; *5*, $LaVO_3$; *6*, $LaCoO_3$; *7*, $LaNiO_3$; *8*, $LaCrO_3$; and *9*, $LaAlO_3$.

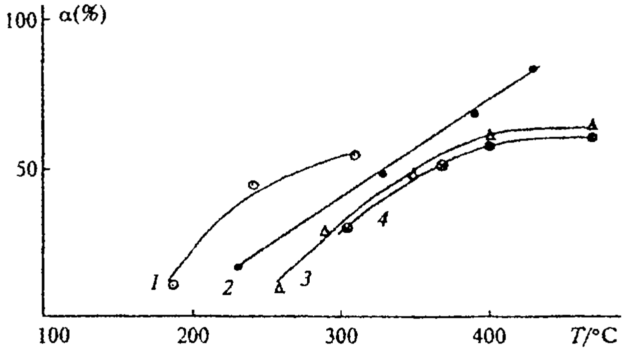

Fig. 2. Temperature effect on the C_3H_6 conversion (α) on different catalysts: *1*, $LaCoO_3$; *2*, $LaCrO_3$; *3*, $LaMnO_3$; and *4*, $LaAlO_3$.

The nature of the catalyst exerts the same effect on the oxidation of propylene as on the reactions of CO and EB. $MCoO_3$ (M is REE) are the most active catalysts.

Additional information on the oxidation process was obtained by comparison of the catalytic properties of complex oxides with different structures (manganites with spinel-like structure and perovskites) under conditions of the pulse regime.

The solid surface during the interaction with the reaction mixture can be characterized by reactions in the pulse regime.[8,9] These reactions proceed under nonsteady-state conditions. The catalysts possess, as a rule, a higher activity and the reactions start at lower temperatures than in the case of the steady-state regime.

Comparison of the data for complete oxidation of CO in the flow and pulse regimes (Table 3) showed that oxidation of CO on manganites (spinel-like structure)

Table 3. Parameters of CO oxidation on complex oxides in the flow (I) and pulse (II) regimes

Catalyst	T_c/°C		T_{max}/°C	α_{max} (%)
	I	II		
$CuMn_2O_4$	90*	80–85	80–85	100
$MgMn_2O_4$	220*	185*	185	100
$LaCoO_3$	120	130	130	100
$LaMnO_3$	130	200	150	50
$LaVO_3$	230	315	275	70

Note. The following designations were used: T_c is the temperature of overall conversion, T_{max} and α_{max} are the temperature and degree of maximum conversion of CO into CO_2 in the pulse regime. * Lit. data.[6]

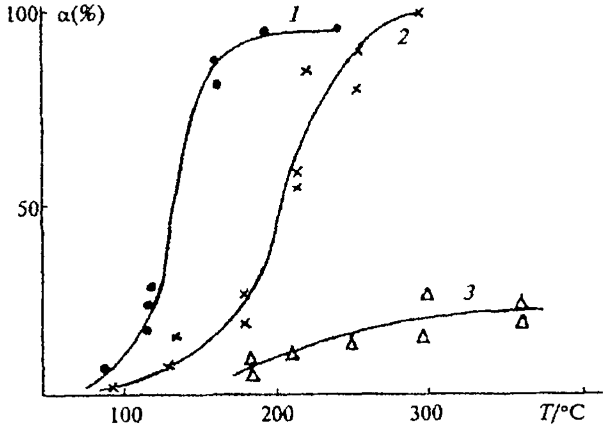

Fig. 3. Temperature effect on the O_2 conversion (α) during its interaction in the pulse regime with different catalysts: *1*, $LaCoO_3$; *2*, $LaMnO_3$; and *3*, $LaVO_3$.

under conditions of the nonsteady-state pulse regime occurs at lower temperatures. At the same time, in this regime on all perovskites studied, a complete conversion of CO is achieved at higher temperatures as compared to the steady-state flow regime.

To reveal the reasons for this phenomenon, we studied the interaction of gases with the catalyst surface, which can be considered as the initial stage of reactions of the gas with the solid.

As follows from Fig. 3, when air pulses interact with the catalyst surface, O_2 is adsorbed in the region of temperatures corresponding to those of the CO oxidation. As the temperature increases, the amount of adsorbed O_2 increases. More active catalysts adsorb greater amounts of O_2.

A similar phenomenon was also observed with the action of a pulse containing CO and air (Fig. 4, *a*,*b*). As the temperature increases, the amount of CO and O_2 converted on perovskites increases. However, it does not correspond to the amount of CO_2 formed. This suggests that the oxidation of CO on perovskites is preceded by the adsorption of CO and O_2 by the catalyst. The same effect was observed for the spinel samples (Fig. 4, *c*). It is noteworthy that the degree of conversion of CO into CO_2 for manganites almost coincides with the overall conversion of carbon monoxide with a temperature increase to 300 °C (see Fig. 4, *c*). The participation of lattice oxygen in the oxidation at high temperatures has previously[6] been established. It is seen in Fig. 4, *a*,*b* that

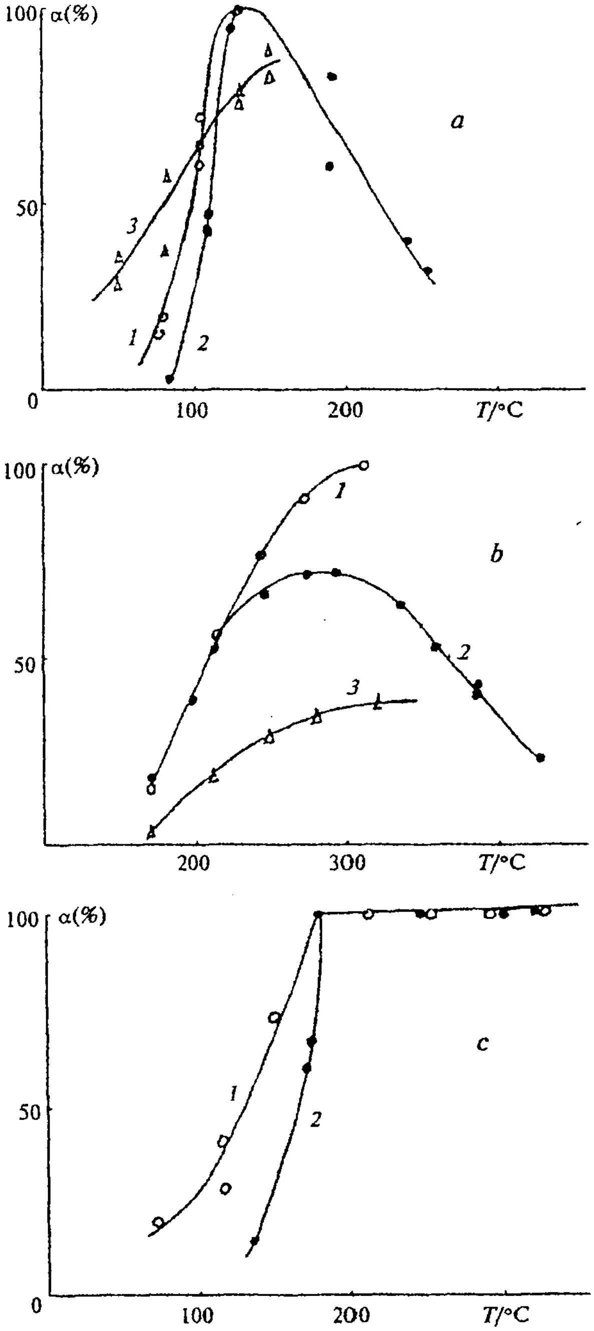

Fig. 4. Temperature effect on the overall CO conversion (*1*), its conversion into CO_2 (*2*), and the O_2 conversion (*3*) in the pulse regime on the catalysts $LaCoO_3$ (*a*), $LaVO_3$ (*b*), and $MgMn_2O_4$ (*c*).

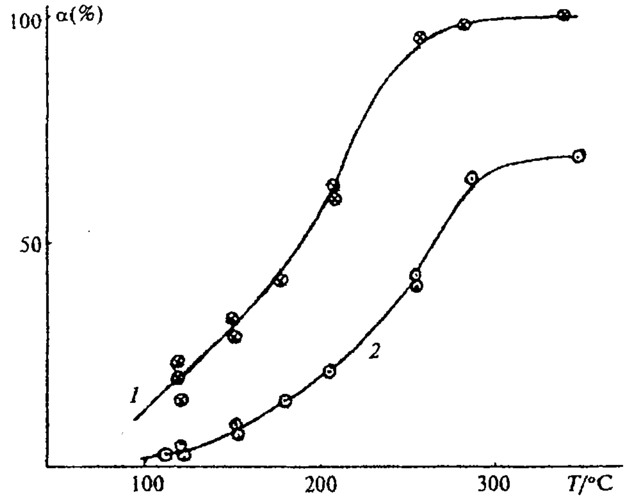

Fig. 5. Temperature effect on the overall CO conversion (*1*) and its conversion into CO_2 (*2*) on the $LaMnO_3$ catalyst in the pulse regime.

the temperature dependence of the degree of CO conversion into CO_2 over perovskites has a maximum. At high temperatures, the complete oxidation of CO into CO_2 on low-activity perovskites is not achieved (see Fig. 4, *a*,*b*, Table 3). Probably, in this case, oxidation is complicated by other reactions of CO, for example, disproportionation: $2\ CO = C + CO_2$. The possibility of the occurence of the carbonate form of CO adsorption has been found.[10] It follows[11] from the results on temperature-programmed desorption that the perovskite surface contains centers with T_{max} ~200—400, ~350, and ~680 °C, which strongly bind 70—95% CO. Thus, it can be assumed that both the oxidation centers and centers of side reactions are present on perovskites.

The study of the temperature effect on the interaction of CO pulses with the $LaMnO_3$ complex oxide surface showed that both the overall conversion of CO and its conversion into CO_2 increase with temperature increase (Fig. 5). The stoichiometry of CO conversion does not correspond to the oxidation of CO to CO_2. Carbon monoxide is most likely adsorbed strongly by the catalyst surface. It has been established[12] that this absorption can result in the formation of new phases on the oxide surface, particularly at high temperatures. The participation of lattice oxygen in oxidation, which was taken into account for manganites,[6] is not important for perovskites. It has also been observed[10] that the spinel surface contains more active centers of oxidation than the perovskite surface. Perhaps, this is the reason for the lower activity of perovskites as compared to that of manganites with the spinel-like structure.

Thus, under conditions of the pulse regime, when the supply of oxygen from the reaction zone to the perovskite surface is deficient, the contribution of side processes can be substantial especially at high temperatures. The catalytic centers responsible for these processes can be more active than oxidation centers. Therefore, the oxidation temperatures on perovskites in the pulse regime are higher than those under flow-type conditions.

Analysis of the results of catalytic studies in the flow-type regime and the data on the interaction of CO with the catalyst surface in the pulse regime exhibits a correlation between the adsorption and catalytic properties of perovskites. Based on this, a "fused" mechanism of the oxidation can be proposed, which assumes the interaction of adsorbed molecules of the oxidized substance with adsorbed oxygen molecules.

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