Catalytic oxidation of CO, hydrocarbons, and ethyl acetate over perovskite-type complex oxides

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

Institute of Physical Chemistry, Russian Academy of Sciences,
117915 Moscow, 31 Leninsky prosp., Russian Federation.
Fax: +7 (095) 952 7514

The catalytic activity of $M^{I}M^{II}O_3$ perovskite-type complex oxides (M^{I} = La, Y, Nd, Yb; M^{II} = Co, Mn, Ni) in the oxidation of CO, propylene, benzene, ethylbenzene, *o*-xylene, and ethyl acetate was investigated. The Co-containing catalysts were shown to be more active in the oxidation than the Mn-containing catalysts. A relationship between the catalytic and adsorption properties was established.

Key words: catalytic oxidation, perovskites, carbon monoxide, hydrocarbons, chemisorption.

Wastes from the chemical industry, motor vehicles, power plants, *etc.* are important atmospheric contaminants. Catalytic oxidation can be used for the elimination of toxic substances from these wastes. Nowadays, a search for new efficient and low-cost catalysts instead of the highly efficient but expensive catalysts based on platinum-group metals is in progress.

Perovskites have been previously shown to be highly active in catalyzing various reactions, *e.g.*, in the oxidation of CO,[1] NH_3,[2] CH_4,[3] in synthesis gas conversion,[4] *etc.* The advantages of complex oxides over simple oxides are well known.[5]

In the present paper the catalytic activity of $M^{I}M^{II}O_3$ perovskite-type complex oxides (M^{I} = La, Y, Nd, Yb; M^{II} = Co, Mn, Ni) was studied.

The oxidation reactions of CO and certain organic compounds (propylene, benzene, ethyl acetate, ethylbenzene, and *o*-xylene) were used as model reactions.

Experimental

The procedure for catalyst preparation was similar to that previously reported.[6] Nitrates of the corresponding metals were used as starting compounds. Nitrates of rare-earth elements were dissolved in a minimum amount of water, an equimolar amount of the second salt and then oxalic acid were added to the solution obtained. The mixture was dried and calcined at 700 °C.

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

The specific surface of the samples was determined by the BET method using low-temperature krypton adsorption. The chemisorption of the gases was studied with a volumetric adsorption set-up. Before the measurements, the samples were treated for 6 h at 400 °C and 10^{-5} Torr. The temperature-programmed CO desorption was carried out chromatographically: Ar, linearly increasing temperature (20—900 °C, 20 °C min^{-1}).

The oxidation of carbon monoxide and propylene was studied in two modes: the flow mode (volume rate 900 h^{-1}) and the pulse mode (pulse volume 1 mL). A LKhM-72 chromatograph (catharometer as the detector, 1 m×3 mm column packed with 5 Å molecular sieves, helium as the carrier gas, 25 °C) was used to monitor CO and C_3H_6 concentrations. The catalyst volume was 2 cm^3.

The catalytic oxidation of liquid organic compounds (0.1 mol m^{-3}) with air oxygen was carried out in a KL-1 unit using the flow mode. The content of organic compounds was determined chromatographically (Tsvet-1 chromatograph, flame ionization detector, 2 m×3 mm column packed with tricresyl phosphate on celite-545, 90 °C). Conditions for CO_2 analysis: catharometer as the detector, 2 m×3 mm column packed with Polysorb-1, 25 °C. The catalyst was used as 1—2 mm granules, the samples weighed ~1.0 g (1 cm^3).

Results and Discussion

The physicochemical parameters of the catalysts obtained are given in Table 1. The specific surfaces of the oxides are not large, but perovskites can adsorb up to 20 μmol m^{-2} CO. IR spectroscopy was used to confirm the existence of the perovskite structure. Perovskites are known[7,8] to have intense absorption bands in the regions of 700—600 and 500—400 cm^{-1}. Absorption at 700—600 cm^{-1} is due to the vibration of the M—O bond when M is in octahedral coordination, while the band at 500—400 cm^{-1} results from M^{I}—O—M^{II} valence vibrations. The IR spectra of the oxides obtained display bands typical of perovskites. For example, Fig. 1 presents the spectrum of $LaMnO_3$ with typical intense bands at 400 and 615 cm^{-1}. The simple oxide La_2O_3 has absorption bands at 388, 648, and 856 cm^{-1}, and Mn_2O_3 has bands

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 602—605, April, 1994.

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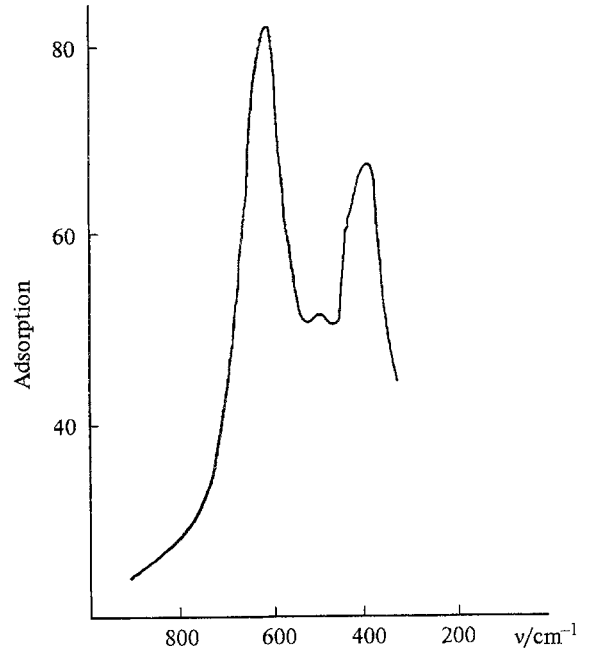

Fig. 1. IR spectrum of $LaMnO_3$.

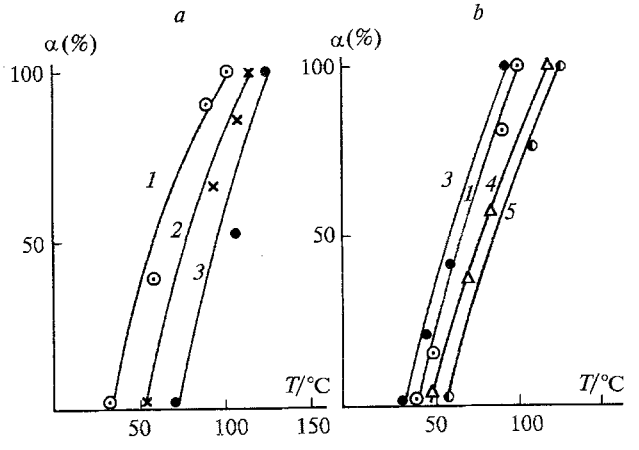

Fig. 2. Plot of the degree of CO conversion (α) *vs.* temperature under flow (*a*) and pulse (*b*) reaction conditions: *1*, $LaCoO_3$; *2*, $YCoO_3$; *3*, $NdCoO_3$; *4*, $LaMnO_3$; *5*, $YMnO_3$.

Table 1. Physicochemical properties and activity of perovskites in CO oxidation

Catalyst	S_{sp} /$m^2\ g^{-1}$	Q_{CO}* /μmol m^{-2}	T_{CO}** Pulse mode	T_{CO}** Flow mode
$LaCoO_3$	4.7	13.8	100	130
$YCoO_3$	3.7	16.2	105	105
$NdCoO_3$	0.1	20.0	90	120
$YbCoO_3$	2.5	12.0	100	145
$LaMnO_3$	1.1	2.4	130	150
$YMnO_3$	14.7	8.5	125	150
$NdMnO_3$	11.3	6.2	100	160
$YNiO_3$	3.0	5.6	Not active	

Q_{CO}* is the amount of CO chemisorbed at 100°C.
T_{CO}** is the temperature of 100% CO conversion.

at 524, 580, and 648cm^{-1}. Other catalysts were also shown to have the perovskite structure, although additional low-intensity bands typical of simple oxides were observed for some samples.

The oxidation of CO was carried out in the pulse and flow modes. A mixture of CO (5—6%) with air (94—95%) was used as the starting gas. Figure 2 plots the degree of conversion *vs.* temperature. The curves obtained are similar to those reported previously.[1,7] To compare the activity of the catalysts, the temperatures corresponding to 100% CO conversion are given in Table 1. 100% conversion is achieved at lower temperatures in the pulse mode than in the flow mode. It is worth noting that stable operation of the catalysts in the flow mode was maintained for several days. The Co-containing catalysts were more active than Mn-containing oxides, and nickelates were catalytically inactive in the temperature range studied. The nature of the rare-earth element had only a slight effect on the oxidation. The catalysts studied can be arranged in the following series of decreasing activity: $LaCoO_3 > LaMnO_3$, $YCoO_3 > YMnO_3 \gg YNiO_3$, $NdCoO_3 > NdMnO_3$.

The chemisorption of CO is greater on more active catalysts (Table 1). A similar dependence was observed for O_2 chemisorption. For example, Fig.3 shows the isotherms of O_2 adsorption on $LaCoO_3$, $LaMnO_3$, $YCoO_3$, and $YMnO_3$. As can be seen from this figure, the more active Co-catalyst adsorbs more O_2 than the less active Mn-containing sample.

The more active catalysts adsorb CO and O_2 to a greater extent, which allows us to make the assumption that these reagents interact in the adsorbed state. The "percussion mechanism" involving the interaction of adsorbed O_2 with CO from the gas phase is not very likely with the catalysts used.

The adsorption behavior of the catalysts was also studied by the CO thermodesorption method using two catalyst pairs, $LaCoO_3$—$LaMnO_3$ and $NdCoO_3$—$NdMnO_3$. Every thermodesorption spectrum had three peaks indicating the existence of three types of CO

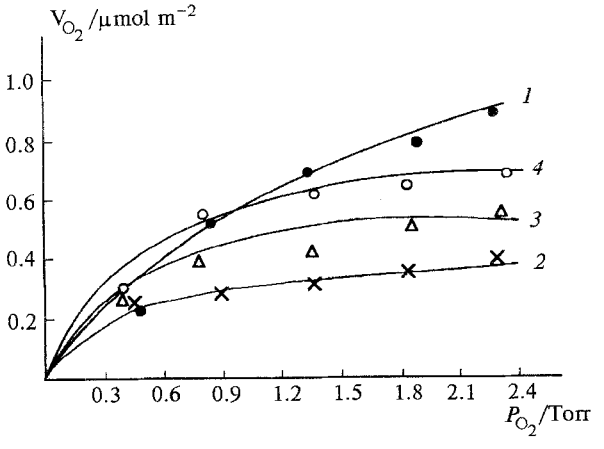

Fig. 3. Adsorption isotherms of O_2 on $YCoO_3$ (*1*), $YMnO_3$ (*2*), $LaMnO_3$ (*3*), and $LaCoO_3$ (*4*).

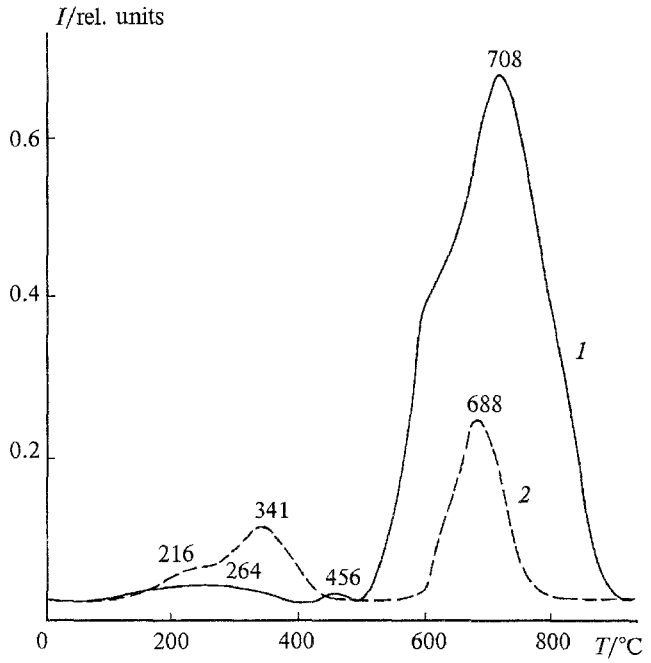

Fig. 4. Spectra of CO thermodesorption from $LaCoO_3$ (*1*) and $LaMnO_3$ (*2*) catalysts.

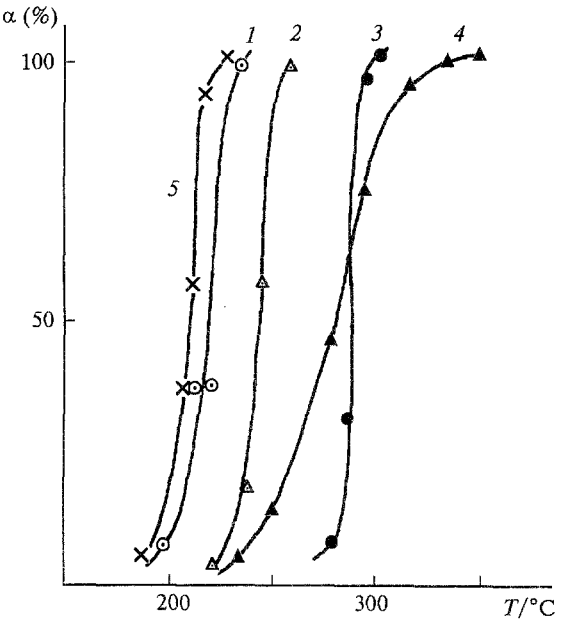

Fig. 5. Effect of temperature on the degree of conversion of organic compounds on $YMnO_3$ (*1—4*) and $LaCoO_3$ (*5*): *1*, ethyl acetate (15400 h^{-1}); *2*, ethylbenzene (6000 h^{-1}); *3*, *o*-xylene (5700 h^{-1}); *4*, benzene (6100 h^{-1}); *5*, ethylbenzene (5900 h^{-1}).

adsorption (Fig. 4, Table 2). The wide temperature range of CO desorption suggests the energetic heterogeneity of the catalyst surfaces.

The desorption kinetics obeys a second-order equation. The activation energy of CO desorption is ~45 kJ mol^{-1} (peak III) for Co-catalysts and ~70—80 kJ mol^{-1} for Mn-catalysts.

Analysis of the thermodesorption spectra allows the conclusion to be made that the adsorption centers of the more strongly bonded CO forms having $T_{max} > 680$ °C are mainly present on the surface of the more active Co-catalysts, where the fraction of these forms is 96—97 %. The fraction of these centers on Mn-catalysts does not exceed 70 %. Therefore, it may be assumed that the centers where strong CO adsorption occurs participate in its oxidation.

Propylene oxidation was carried out on the most active catalysts under flow reactor conditions. The starting gas contained 5 mol. % C_3H_6. The temperatures of 100 % propylene oxidation are given in Table 3. These data show that this process occurs at higher temperatures than CO oxidation. However, in both cases the Co-containing catalysts were more active than their Mn-containing counterparts.

Complex oxides possessing the perovskite structure were also tested in the oxidation of ethyl acetate and certain aromatic hydrocarbons very frequently found as toxic components of industrial gases. In this case, carbon dioxide was the only carbon-containing reaction product.

Table 2. Spectra of CO thermodesorption from the surfaces of perovskite-type catalysts

Catalyst	T_{max}/°C	Peak area (%)
$LaMnO_3$	264	15
	341	27
	688	58
$LaCoO_3$	264	3
	456	1
	708	96
$NdMnO_3$	120	4
	300	27
	739	69
$NdCoO_3$	216	2
	360	1
	762	97

Table 3. Propylene oxidation in the presence of perovskite-type catalysts

Catalyst	$T_{C_3H_6}$/°C*
$YCoO_3$	350
$YbCoO_3$	440
$NdMnO_3$	480
$YMnO_3$	475

* $T_{C_3H_6}$ is the temperature of 100 % propylene conversion.

The oxidation of ethyl acetate on $YMnO_3$ occurs rapidly at relatively low temperatures, 190—230 °C (Fig. 5). Deep oxidation of aromatic hydrocarbons proceeds at 230-350 °C. Benzene conversion increases slowly with an increase in temperature, and benzene readily undergoes oxidation only at $T > 300$ °C. An increase in the volume flow rate to ~15000 h^{-1} has almost no effect on the oxidation conversion. For comparison, Fig. 5 presents data on the oxidation of ethylbenzene on a Co-containing sample. In this case the temperature range of conversion was lower than with the Mn-catalyst, and complete oxidation was observed at 235 °C.

The catalytic activity of the samples in the oxidation of CO and in the deep oxidation of organic compounds indicates that these processes occur on the same sites of catalyst surfaces.

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Received April 22, 1993