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Cerium Substituted Lanthanum Perovskites $La_{1-x}Ce_xMO_3$ (M = Co, Fe, Mn) as Catalysts for the CO + NO Reaction*

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Since 1970, perovskite-type oxides have been suggested as substitutes for noble metals in electrocatalysis [1] and in automotive exhaust catalysis [2]. Encouraging results were obtained with $LaMnO_3$ and $LaCoO_3$ in CO oxidation and NO reduction.

These compounds, of general formula ABO_3, usually include a lanthanide element A and a transition metal B. These oxides are very interesting since they allow partial substitution of A and B ions without important modification of the perovskite structure. Therefore, isostructural series like $A_{1-x}A'_xBO_3$ or $AB_{1-y}B'_yO_3$, with different physical and catalytic properties, can be synthesized.

On the other hand, cerium is a well known additive of exhaust catalysts. Its oxygen storage ability is used to broaden the air/fuel ratio window; hence it improves the activity of three way catalysts (CO, hydrocarbon oxidation, NO reduction).

Therefore, $La_{1-x}Ce_xMO_3$ perovskites (M = Co, Fe, Mn) are expected to show promising catalytic properties as automotive exhaust catalysts.

Experimental

Catalyst Preparation

$La_{1-x}Ce_xMO_3$ compounds were synthesized by evaporation of a solution of the respective metal nitrates and calcination of the precursors at 1000 °C for 5 h. In this paper, we present the results obtained for $La_{0.95}Ce_{0.05}MO_3$ ($x = 0.05$) and $La_{0.8}Ce_{0.2}MO_3$ ($x = 0.2$) catalysts.

Characterization

X-ray powder diffraction patterns were recorded on a Philips PW 1730 diffractometer using Ni filtered Cu Kα radiation. XPS spectra were obtained on a Hewlett Packard 5950 A spectrometer with Al Kα radiation.

Catalytic Tests

The catalysts were tested for the CO + NO reaction in a flow reactor system. Before the tests, the compounds (1.0 g) mixed with small glass beads (weight ratio 1:2) were pretreated overnight in N_2 at 400 °C and then in a mixture of CO, NO, N_2 and Ar for 30 min at the same temperature to attain steady-state conversion. The same flowrate ($Q = 150$ ml/min), the same mixture of reagents (20% mol CO, 20% mol NO, 20% mol Ar, N_2) and the same reaction temperature ($T = 300$–500 °C) were used to compare the activity of the different catalysts.

Results and Discussion

X-ray Diffraction

Since no traces of La_2O_3 appear in the diffraction patterns, the $LaMO_3$ perovskite phase must be completely formed at 1000 °C. On the other hand, the cerium introduced in the reagents is not totally incorporated in the perovskite lattice. The excess crystallizes as CeO_2 in similar quantities, whatever the transition metal (Table I). Moreover, there are no traces of CoO or Fe_2O_3 neither in $La_{0.95}Ce_{0.05}MO_3$ nor in $La_{0.8}Ce_{0.2}MO_3$ (M = Co, Fe), except for small amounts of Mn_3O_4 in $La_{0.8}Ce_{0.2}MnO_3$. We can therefore suppose the presence of A-site cation vacancies in the perovskite structure, and can formulate the catalysts as $La_{1-x}Ce_y\phi_{x-y}MO_3$ (ϕ = A-site cation vacancy, with $1 > x > y > 0$).

X-ray Photoelectron Spectroscopy

(a) Determination of the valence state of the ions

In the ABO_3 perovskite structure, the A and B elements are normally A^{3+} and B^{3+} ions, but substitution in the A site can modify the oxidation state of B. By XPS, we can determine that all the transition metals are introduced as M^{3+} ions in the perovskite lattice. In $La_{0.95}Ce_{0.05}MO_3$ catalysts, some cerium is incorporated as Ce^{3+}, but the predominant Ce^{4+} species belongs to the CeO_2 phase in excess. On the other hand, the Ce 3d spectra of $La_{0.8}Ce_{0.2}MO_3$ compounds are very similar to those of CeO_2 (Fig. 1).

TABLE I. Relative Heights of X-ray Diffraction Peaks Characterizing the Different Catalysts

	I_1	I_2	I_3
$La_{0.95}Ce_{0.05}MO_3$	0.058	0.041	0.058
$La_{0.8}Ce_{0.2}MO_3$	0.27	0.21	0.31

$I_1 = I(CeO_2)$ ($d = 3.16$ Å)/$I(LaCoO_3)$ ($d = 2.67$ Å). $I_2 = I(CeO_2)$ ($d = 3.16$ Å)/$I(LaFeO_3)$ ($d = 2.78$ Å). $I_3 = I(CeO_2)$ ($d = 3.16$ Å)/$I(LaMnO_3)$ ($d = 2.72$ Å).

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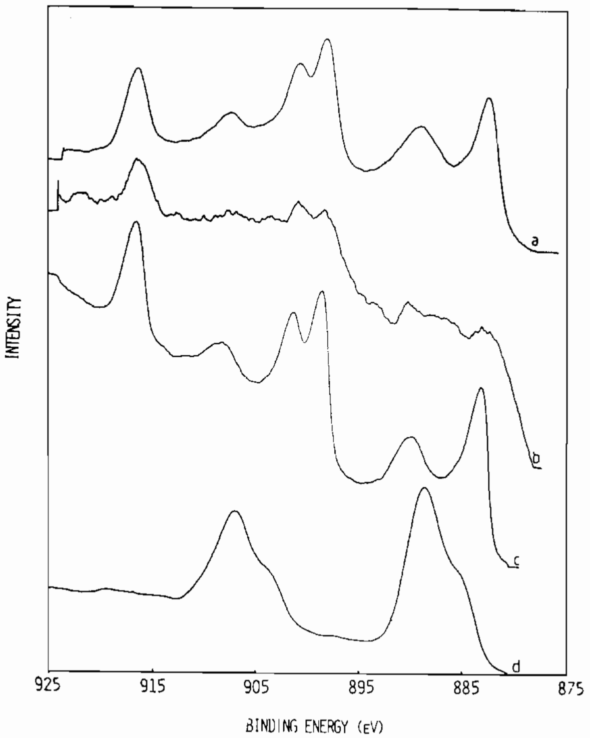


Fig. 1. Comparison of the Ce 3d spectra of (a) $La_{0.8}Ce_{0.2}CoO_3$, (b) $La_{0.95}Ce_{0.05}CoO_3$, (c) CeO_2 [Ce^{4+}], (d) $Ce_2(C_2O_4)_3 \cdot xH_2O$ [Ce^{3+}].

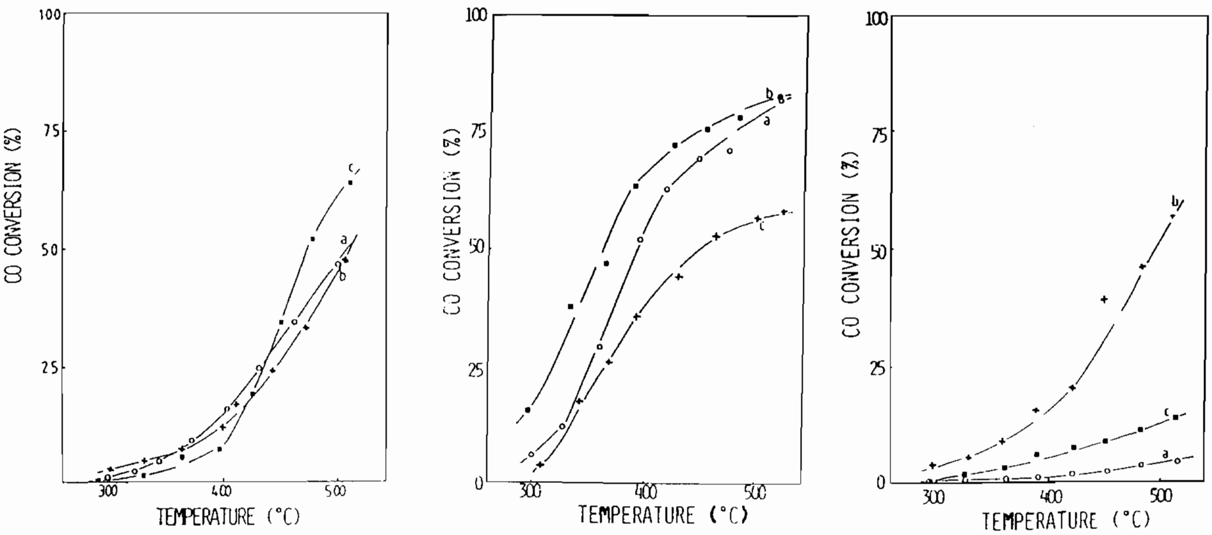
(b) Ce/La and M/La atomic ratios calculated by XPS

The surface atomic ratios were calculated from the La 3d, Ce 3d and M 2p core peak intensities. In Table II, we see that most observed M/La ratios are similar to the value used in the synthesis, indicating that the perovskite is formed without excess metal oxide MO_x (M = Co, Fe, Mn) at the surface.

The Ce/La atomic ratios for the different catalysts are shown in Table III. In $La_{0.95}Ce_{0.05}MO_3$ compounds, cerium is mainly at the surface of the catalysts (Ce/La (XPS) > Ce/La (synthesis)). On the other hand, in $La_{0.8}Ce_{0.2}MO_3$ catalysts, cerium, mainly as CeO_2, and the perovskite are mixed together without any migration effect of one of these phases to the surface, since the calculated ratios are similar to the synthesis ratios.

TABLE II. Atomic Ratios from XPS La 3d and M 2p Peak Intensities

	Co/La	Fe/La	Mn/La	M/La_{synt}
$La_{0.95}Ce_{0.05}MO_3$	0.61	0.68	1.02	1.05
$La_{0.8}Ce_{0.2}MO_3$	1.02	1.30	1.10	1.25



(a) $LaCoO_3$

(b) $La_{0.95}Ce_{0.05}CoO_3$

(c) $La_{0.8}Ce_{0.2}CoO_3$

(a) $LaFeO_3$

(b) $La_{0.95}Ce_{0.05}FeO_3$

(c) $La_{0.8}Ce_{0.2}FeO_3$

(a) $LaMnO_3$

(b) $La_{0.95}Ce_{0.05}MnO_3$

(c) $La_{0.8}Ce_{0.2}MnO_3$

Fig. 2. CO oxidation by NO over $La_{1-x}Ce_xMO_3$ catalysts.

TABLE III. Atomic Ratios Ce/La from XPS La 3d and Ce 3d Peak Intensities

	R_1	R_2	R_3	R_{synt}
$La_{0.95}Ce_{0.05}MO_3$	0.10	0.11	0.12	0.052
$La_{0.8}Ce_{0.2}MO_3$	0.26	0.27	0.29	0.25

R_1 = Ce/La (XPS) for M = Co. R_2 = Ce/La (XPS) for M = Fe. R_3 = Ce/La (XPS) for M = Mn.

Catalytic Tests

The activity of the catalysts with different transition metals and different quantities of cerium are compared in Fig. 2. For the $La_{1-x}Ce_xCoO_3$ compounds, the quantity of cerium introduced does not significantly modify the catalytic activity of the catalyst. But in the $La_{1-x}Ce_xFeO_3$ series, the maximum activity is obtained for $x = 0.05$ and the introduction of more cerium has a negative effect on NO reduction by CO. Among the Mn perovskites, $LaMnO_3$ appears to have very little activity but, among the $La_{1-x}Ce_xFeO_3$ compounds the best catalyst is obtained with $x = 0.05$.

Conclusions

X-ray diffraction patterns have revealed that cerium is not entirely introduced in the perovskite lattice, and that the excess forms a CeO_2 phase. Since no transition metal oxides are detected, we assume the presence of A-site cation vacancies in the structure. From XPS, we can identify Ce^{3+} ions in the perovskite structure ($x = 0.05$) and correlate this with the maximal catalytic activity obtained for $La_{0.95}Ce_{0.05}MO_3$. Among the transition metals, Fe appears to be the more suitable for the CO + NO reaction.

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References

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2 W. F. Libby, *Science, 171*, 499 (1971).