the Gulf Coast of the United States by Hicks (*6*) and Meade and Emery (*7*) and along the West Coast by Roden (*10*) and Saur (*11*).

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Rare-Earth Oxides of Manganese and Cobalt Rival Platinum for the Treatment of Carbon Monoxide in Auto Exhaust

Abstract. *The perovskite-like compounds $RE_{1-x}Pb_xMnO_3$ and $RECoO_3$, where RE (rare earth) is lanthanum, praseodymium, or neodymium, are active catalysts for the oxidation of carbon monoxide. Crushed single crystals of these compounds compare favorably with commercial platinum catalysts in initial activity and lifetime. Therefore, these compounds are promising substitutes for platinum in devices for the catalytic treatment of auto exhaust.*

Recently, mixed oxides of cobalt, namely, $La_{0.8}Sr_{0.2}CoO_3$ and $LaCoO_3$, have been described as active catalysts for electrode oxidation-reduction reactions (*1*) and hydrogenation reactions (*2*), respectively. It has been suggested that $LaCoO_3$ might be a good catalyst for the treatment of auto exhaust gases (*2*). We have tested this compound, and others with the same perovskite-like crystal structure, in the oxidation of CO, the main toxic constituent of automotive exhaust. The compounds $LaCoO_3$ and $PrCoO_3$ were found to be active catalysts for the oxidation of CO. The manganites $La_{1-x}Pb_xMnO_3$ and $Pr_{1-x}Pb_xMnO_3$, but particularly $Nd_{1-x}Pb_xMnO_3$, with $0.4 < x < 0.6$, were very active also. The presence of Pb in these compounds led us to measure the poisoning of the activity by Pb derived from gasoline additives. This was not as severe a problem as with other catalysts. The cobaltites and manganites compare favorably with commercial Pt catalysts, which were tested under the same conditions (Table 1). They show initial activities similar to that of the PTX catalyst (Engelhard), which was designed for exhaust treatment (*3*). The activities of the manganites deteriorate considerably more slowly than that of Pt. Therefore, these compounds seem very promising substitutes for Pt in catalytic devices for the treatment of auto exhaust.

The test reaction was the oxidation of CO with O_2. In a continuous flow system a mixture of CO and O_2 (2 : 1 molar ratio) was fed (30 ml/min) through a charge of approximately 2 cm³ of catalyst. The effluent from the reactor was automatically sampled at intervals of 2 minutes or more, and analyzed by means of a gas-liquid chromatograph with an automatic integrator. The conversion of CO was determined as a function of temperature while the catalyst was slowly heated up. The activities of the fresh catalysts are given in Table 1 as the temperatures at which 5, 10, or 20 percent conversion of CO was reached, normalized for a 3-g charge of catalyst. The deactivation of the catalysts with time was subsequently followed at constant temperature (Table 1). The

Table 1. Activity and lifetime of oxidation catalysts for the test reaction: $CO + \frac{1}{2}O_2 \rightarrow CO_2$. Flow rate: 30 ml/min of a stoichiometric mixture at normal temperature and pressure.

Catalyst*	S‡ (m²/g)	Activity test†				Life test			
		Weight of catalyst (g)	Temperature (°C) for CO conversion of			Time (hours)	Temperature (°C)	Conversion§	
			5%	10%	20%			Beginning (%)	End (%)
Pt (PTX)	7.0	1.2	185	205	225	77	235	11	5.9
Pt (PTX)	7.0	0.91	177	197	222	56	235	8.5	6.4
Pt (0.5% on Al_2O_3)	110	0.94	80	160					
$La_{1-x}Pb_xMnO_3$ (sample 1)	< 0.1	2.8	190	215	245				
$La_{1-x}Pb_xMnO_3$ (sample 2)	< 0.1	5.1	183	205	233	136	330	68	44
$Pr_{1-x}Pb_xMnO_3$	< 0.1	3.5	198	225	247				
$Nd_{1-x}Pb_xMnO_3$	< 0.1	3.4	165	180	195	60	208	22	13
$LaCoO_3$ (sample 1)	< 0.1	4.4	180	200					
$LaCoO_3$ (sample 1)	< 0.1	3.7	183	196	215	15	210	20	6.5
$LaCoO_3$ (sample 2)	< 0.1	5.6	187	197	208	25	200	18	9.3
$LaCoO_3$ (sample 2)	< 0.1	4.6	190						
$PrCoO_3$	< 0.1	3.7	160	175		60	212	16	11

* The atomic fraction x in the manganites may vary between 0.4 and 0.6. All oxides listed are crushed single crystals. † Conversions are normalized for 3 g of catalyst, on the assumption that the reaction rate is first order with respect to CO and O_2. At these relatively low conversions, the error involved is slight. ‡ Specific surface area was determined with the Shell/Perkin-Elmer Sorptionmeter. From the size of the single crystal particles, a specific surface area of 0.03 m² per gram of catalyst was calculated for the rare-earth oxides. § Conversions at the beginning and end of the test are for the actual weight of charge in column 3.

fact that the test reaction was highly exothermic made temperature control difficult. Control to within ± 3°C was achieved with an automatic controller (Leeds & Northrup) by maintaining the catalyst in a fluidized state through vibration of the reactor. The reactor was suspended in a fluidized bed which served as the heat-transfer medium.

A series of polycrystalline perovskites was prepared by sintering mixtures of the constituent oxides. The products were shown by x-ray diffraction measurements to be single phase. Samples of $LaMnO_3$, $LaCrO_3$, and $LaCoO_3$ were of comparable activity in the CO oxidation, whereas $LaVO_3$ deteriorated rapidly and $LaFeO_3$ was considerably less active than the other oxides.

The oxide catalysts used most extensively were crushed single crystals. X-ray diffraction measurements confirmed the perovskite structure and showed that the oxides were single phase. Two Pt catalysts marketed by Engelhard Industries were used for comparison. The PTX catalyst, consisting of approximately 0.5 percent (by weight) Pt on SiO_2-Al_2O_3, was obtained in the form of a ceramic honeycomb structure. A catalyst of 0.5 percent Pt on Al_2O_3 in the form of pellets (0.32 cm) was also used. Both were crushed. For all catalysts a sieve fraction between 37 and 250 μm was used in the reactor.

The results in Table 1 show that $Nd_{1-x}Pb_xMnO_3$ and $PrCoO_3$ were more active than the PTX catalyst, whereas the other manganites and cobaltites were approximately as active as the PTX catalyst. This is the more encouraging since the specific surface area S of these oxides was only 0.03 to 0.1 m^2 per gram of catalyst, whereas the specific surface area of Pt in the commercial catalysts is expected to be of the order of 0.3 m^2 per gram of catalyst. The activity of the 0.5 percent Pt on Al_2O_3 pellets was higher than that of any other catalyst, but it deteriorated rapidly even during the activity test.

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4. We thank J. N. Carides, who cooperated in the construction of the test apparatus, and F. Schrey, who determined the specific surface areas of the catalysts. R. L. Hartless and A. M. Trozzalo conducted some preliminary tests on the reduction of the rare-earth oxides by CO.

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Fig. 1. (A and B) Portions of fossil leaf variants of *Cercidiphyllum* showing remains of spongy mesophyll. (C and D) Portions of cleared long-shoot leaves of modern *Cercidiphyllum japonicum* Siebold and Zuccarini showing lacunose spongy mesophyll. (E) Portion of a fossil leaf compression of *Platanus* showing remains of spongy mesophyll. Fossil specimens A, B, and E bear numbers S 2825, S 1586 (A), and S 169 (L), respectively, of the paleobotanical collection in the Department of Botany, University of Alberta. Magnification: A, B, C, and E, × 25; D, × 200.

Spongy Mesophyll Remains in Fossil Leaf Compressions

Abstract. *Spongy mesophyll tissue has been discovered preserved in fossil leaf compressions. The fossils occur in an outcrop at Genesee, Alberta, Canada. The fossiliferous beds belong to the Edmonton formation of Upper Cretaceous–lower Tertiary age. The mesophyll characteristic, when taken in conjunction with other characteristics, was found useful in the identification of some fossil leaves. Numerous detailed observations as well as comparisons of both living and fossil leaves show that the remains represent neither the epidermal nor the palisade tissue.*

In the course of an intensive investigation of a large suite of carbonized compressions of fossil leaves collected from a single outcrop at Genesee, Alberta, Canada, the discovery was made that portions of the spongy mesophyll were preserved. The fossiliferous beds belong to the Edmonton formation (*1*) and are of Upper Cretaceous–lower Tertiary age. The full significance of the discovery of remains of mesophyll came to light subsequently when comparative morphological studies were made between the compressions and cleared leaves of their presumed modern correlatives. Sixty percent of the fossils comprise deciduous angiosperm leaves of which 43 percent belong to the genus *Cercidiphyllum* and 2 percent belong to *Platanus*.

A pattern of lacunae (Fig. 1, A, B, and E) was observed in more than a hundred compressions of leaf variants of *Cercidiphyllum* and a few fragments of *Platanus*. The lacunae are more or less circular in configuration, and they are easily observed even under low magnification. The lacunae show a wide range of variation in size. On the basis of 50 random measurements in ten specimens, the lacunae show a mean diameter of 75 μm in *Cercidiphyllum* (Fig. 1, A and B) and 30 μm in *Platanus* (Fig. 1E). A remarkably similar pattern was observed in spongy mesophyll tissue in cleared leaves of the living species of *Cercidiphyllum* and *Platanus*. Figure 1, C and D, shows a portion of a cleared long-shoot leaf of *C. japonicum* Siebold and Zuccarini illustrating the highly lacunose spongy mesophyll. In Fig. 1D individual cells encircling the lacunae are seen. One hundred and fifty random measurements of the diameters of lacunae in 20 cleared leaves of both long- and short-shoot leaves of *C. japonicum* showed a wide range of variation with a mean of 80 μm in long-shoot leaves and 45 μm in short-shoot leaves. The presence of lacunose mesophyll in *Cercidiphyllum* was found to be universal, irrespective of the geographical location, the age of the plant, and the type of leaf. The mesophyll lacunae in the leaves of living *P. cuneata* Willdenow were observed to be small, with a mean diameter of 26 μm.

The size and configuration of the lacunae in fossil leaves are very similar to that of the intercellular spaces in the spongy mesophyll tissue seen in the living plant. These observations led me to conclude that the lacunae found in fossil leaves represent the remains of mesophyll tissue (see Fig. 1, A and C).

None of the compressions showed any recognizable cuticular remains. Epidermal cells in the extant species of *Cercidiphyllum* are roughly square to rectangular in shape, are small, and have wavy cell walls. These cells are in no way comparable to the lacunae found in the fossils (Fig. 1, A and B), thus eliminating the possibility that the lacunae might represent the intracellular spaces of epidermal cells. Furthermore,