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Perovskite Oxides: Materials Science in Catalysis

Perovskite oxides, long known in solid-state chemistry and physics, find new applications in catalysis.

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Among the technological problems that require attention today are the chemical conversion of coal into gas, of pollutants into innocuous gases, of water into hydrogen and oxygen, and of air and water into fertilizers. The key to the commercial and economical success of these conversions is catalysis, a research area which draws on scientific and engineering principles to bring about chemical conversions in fluids as a result of contact with certain solid surfaces (*1*).

Catalysis is a multidisciplinary field, in which theoretical chemistry and experimental surface physics combine to produce a rapidly developing and increasingly sophisticated conceptual framework within which the catalytic chemistry at surfaces may be understood (*2*). Solid-state chemistry is also being increasingly brought to bear on the formulation of catalytic materials, opening pathways to the "tailoring" of catalysts (*3*). At the same time, the interdisciplinary field of materials science, touching as it does on the relation between the properties of materials and their macro-, micro-, and atomic structures, provides a natural matrix for the elucidation of structure-property relationships in defect solids used as catalysts (*4*). For example, the same properties that are important in the successful application of electronic materials—crystallinity, grain or particle size, porosity, defect structure, and compositional variation—are crucial for the successful operation of catalysts, whether they be single phase or composites.

In this article we outline the role that perovskites play at this confluence of disciplines. Even though these materials have not yet found application as commercial catalysts, their importance in efforts to correlate solid-state chemistry with catalytic properties, their properties as they depend on preparative methods, and the fact that they can be tailored for specific catalytic demands establish these oxides as prototype models for catalytic materials. Their commercial potential as oxidation-reduction catalysts is at present being explored.

The Versatility of Perovskites

Perovskite oxides, which are structurally similar to the mineral of that name ($CaTiO_3$), have long been studied because of technologically important physical characteristics such as ferroelectricity, piezoelectricity, pyroelectricity, magnetism, high-temperature superconductivity, and electrooptic effects. They are a class of materials of such great versatility that for decades they have served as both the testing and breeding grounds for ideas in solid-state chemistry (*5*). Surprisingly, until recently the perovskites had not attracted much attention in the field of catalysis (*6*). In the last few years the quest for stable and active catalysts for the treatment of automotive exhaust and for electrocatalytic fuel cell electrodes has stimulated interest in this class of compounds.

In 1970 and 1971, cobaltate perovskites were suggested as substitutes for noble metals in electrocatalysis (*7*) and in automotive exhaust catalysis (*8*). Encouraging results were obtained with cobaltate and manganate perovskites in the oxidation of carbon monoxide (CO) and the reduction of nitric oxide (NO) (*9, 10*). At the low CO concentrations representative of a large degree of conversion of CO in auto exhaust, the activity of the manganates and cobaltates is significantly less than that of Pt, however (*11–14*). The sensitivity of these particular perovskites to poisoning by sulfur dioxide (SO_2) later dampened the initial enthusiasm for their application in automotive exhaust catalysis (*12*). In current approaches perovskites substituted with small amounts of noble metals are being used (*13, 15*). Concurrently, solid-state chemists, materials scientists, and theorists have become interested in the interaction of the solid-state and catalytic properties of perovskites so that now catalysis on perovskite-type oxides is a very active area of overlap between their disciplines. Rather than as substitutes of noble metals, the perovskites are now being studied as novel and intriguing catalysts in their own right (*16*).

The general formula of perovskites is ABO_3. Their crystal structure is relatively simple. The B ions may be catalytically active *3d*, *4d*, or *5d* transition metal ions which occupy oxygen octahedrons. These octahedrons share corners in a cubic array (Fig. 1). The A ions, which fit into the dodecahedral interstices, may be large rare-earth, alkaline-earth, alkali, or

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other large ions such as Bi^{3+} or Pb^{2+}. The diverse properties of the perovskites are derived on the one hand from the large variety of A and B ions which fit the structure (Table 1) and on the other hand from the variation in the valence state of the transition metal ions which can be obtained by proper choice of the A ions. Solid solutions of ABO_3 with $A'BO_3$, $AB'O_3$, or even $A'B'O_3$ (A' and B' signify substitution to the A site and B site, respectively) add to the capability of "tailoring" specific properties.

Auto Exhaust Catalysts

The Clean Air Act of 1970 set standards for the emissions of CO, hydrocarbons (HC), and NO in auto exhaust in the United States. The predominant strategy to meet these standards has been and continues to be the use of catalytic converters in the exhaust train (*17*). Perovskite-type oxides of Co, Mn, and Ru have been widely investigated for use in the three types of catalysts designed for these devices (*17*). However, commercial application has yet to be achieved.

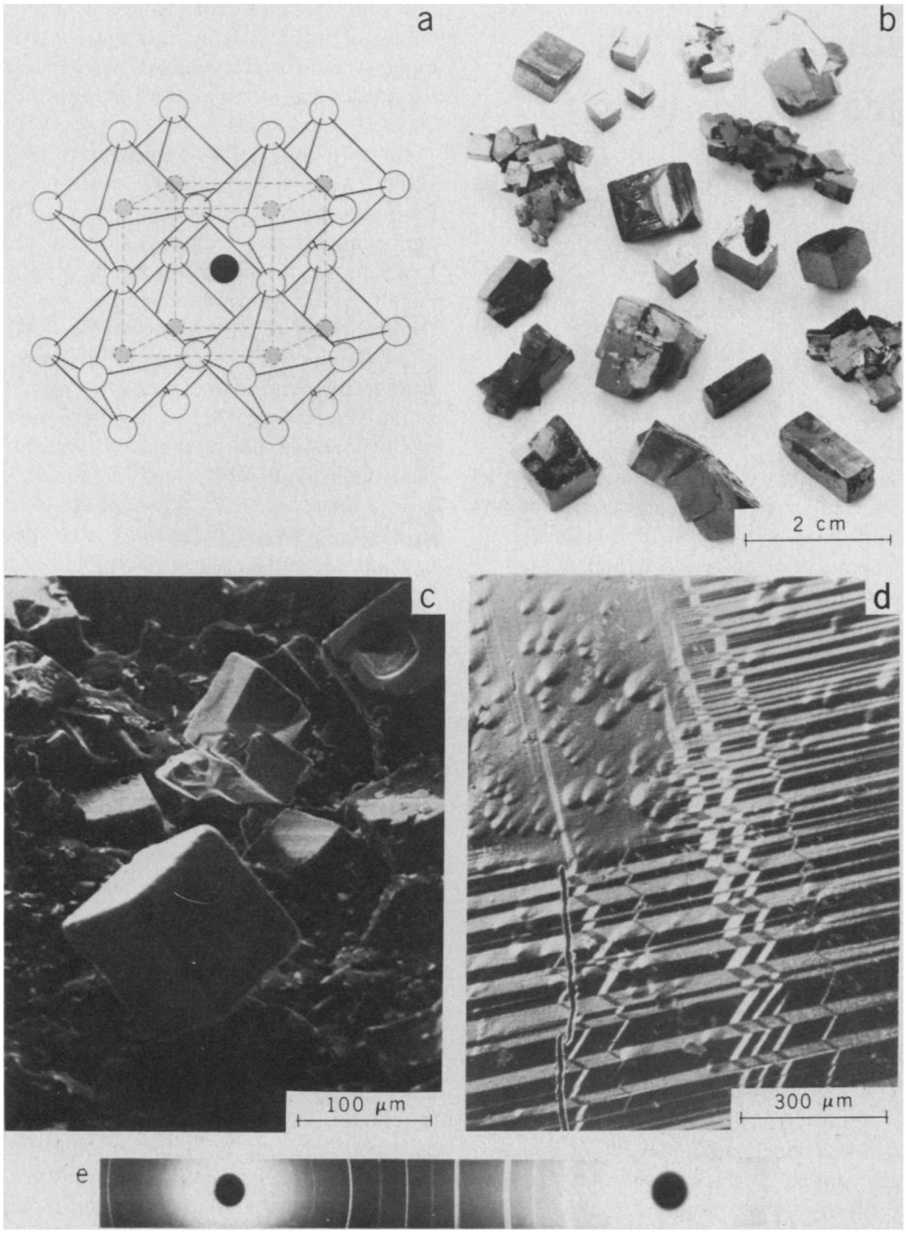


Fig. 1. Structural properties of ABO_3 perovskite oxides. (a) Structural model showing oxygen (open circles) octahedrons containing the B ions (shaded), linked through corners to form a three-dimensional cubic lattice. Eight octahedrons form a cage to fit the A ion (filled circle). (b) Photograph of $\{La_{0.7}Pb_{0.3}\}MnO_3$ crystals grown from a lead borate flux. The cubic morphology reflects the (almost) cubic symmetry of the perovskite lattice. (c) Scanning electron micrograph of small flux-grown $\{La_{0.7}Pb_{0.3}\}MnO_3$ crystals. (d) Surface topography in Nomarski contrast photomicrograph of $\{La_{0.7}Pb_{0.3}\}MnO_3$ crystals. The domain structure may be ferromagnetic in origin. (e) Debye-Scherrer x-ray diffractogram of $\{La_{0.7}Pb_{0.3}\}MnO_3$ powder. The splitting of lines is due to deviation from true cubic symmetry.

The catalytic converter designed for the reduction of NO to N_2 is the first converter to be subjected to the exhaust gases leaving the engine. It thus bears the brunt of the load of catalyst poisons, such as Pb and S derived from the fuel and their compounds produced in the combustion process. Perovskite catalysts have particular promise here because Pb is a common A component in the ABO_3 formula and is not a chemical poison for these catalysts (*18*). For example, $Pb_2Ru_2O_6$, which is related in structure to the perovskites, is nearly as effective for the reduction of NO as the perovskite $SrRuO_3$ (*19*). Exposure of the ruthenates to SO_2 in the reducing conditions prevalent in the NO_x catalyst (NO_x = oxides of nitrogen) can be withstood fairly well (*20*). The ability of many perovskites containing Ru, including $SrRuO_3$, $LaRuO_3$, $\{La_{0.8}K_{0.2}\}[Mn_{0.94}Ru_{0.06}]O_3$ (*21*), and $\{La_{0.8}Sr_{0.2}\}[Co_{0.9}Ru_{0.1}]O_3$, to reduce NO in synthetic gas mixtures (NO, CO, H_2, H_2O, and inert diluent) and in automotive engine exhaust has been studied extensively (*15, 19, 22, 23*). The prime characteristics of these catalysts are a highly selective conversion of NO to N_2 [low yield of ammonia (NH_3)] and high activity. In these respects, these catalysts are similar to Ru metal. The activity per exposed Ru is almost identical for metallic Ru, $SrRuO_3$, and $\{La_{0.8}K_{0.2}\}[Mn_{0.94}Ru_{0.06}]O_3$ (*16*). The advantage of Ru in the perovskites over Ru metal is the dispersion and dilution of Ru in the B sites, which make the catalyst more resistant to losses in efficacy caused by agglomeration and particle growth ("sintering"). The binding of Ru in the perovskite also significantly diminishes the loss of activity resulting from the evaporation of oxides of Ru. To date, perovskites with small amounts of Ru in the B site are among the prime contenders as NO_x catalysts in dual-bed converter designs (*24*). Figure 2a illustrates the effective performance of $\{La_{0.8}Sr_{0.2}\}[Co_{0.9}Ru_{0.1}]O_3$ in reducing NO in engine exhaust from leaded gasoline.

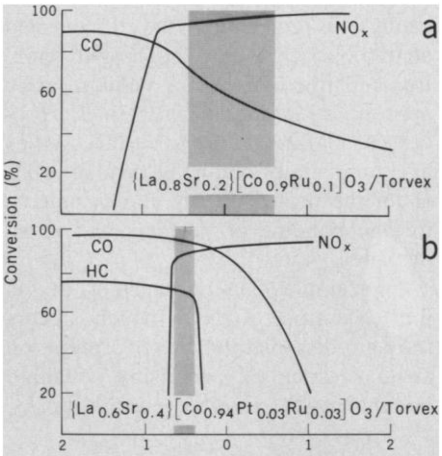
The reduction of NO can be carried out simultaneously with the oxidation of CO and HC if the composition of the exhaust gas is maintained not far from stoichiometric conditions. This requirement may be particularly suitable for perovskite-type catalysts based on Co or Mn, since these oxides show their highest activity for CO oxidation when they are in a slightly reduced state whereas their activity for the reduction of NO is highest in a slightly oxidized state (*16*, *24–26*). One of the metals actively being studied for application in these "three-way" catalysts, Rh (*27*), shows a high activity for the reduction of NO when present in small amounts in the perovskite $\{La_{0.8}K_{0.2}\}[Mn_{0.9}Rh_{0.1}]O_3$ (*23*). Particularly promising is the combination of Ru and Pt at the B site in $\{La_{0.6}Sr_{0.4}\}[Co_{0.94}Pt_{0.03}Ru_{0.03}]O_3$ (*15*). These two metals, chosen for selective reduction of NO to N_2 at the reducing side and efficient oxidation of CO and HC at the oxidizing side of the stoichiometric range, provide an operating window (shaded area in Fig. 2b) in which the conversions of all three pollutants are quite high. At present, it is not clear whether the auto industry will use either Ru or Rh for the control of NO in automotive exhaust catalysts. Both metals are in short supply. Perovskites with Ru or Rh in the B site would have to be dispersed on a carrier oxide to provide economical usage of the noble metals. In the work at DuPont (*15*), active catalysts were prepared which meet this condition.

In current catalytic systems [and in the dual-bed system (*17*)] the concentrations of CO and HC emissions are kept below legislated standards by an oxidation catalyst on which these compounds are converted into CO_2 and H_2O with air added to the exhaust mixture. Although the noble metal technology based on the use of Pt-Pd oxidation catalysts is already well developed, perovskites may offer an economical alternative which conserves the resources of noble metals. Figure 3 illustrates the high activity that can be attained with perovskites of Cu and Mn (*28*, *29*). Perovskite catalysts, like other oxide catalysts, can be poisoned by S that occurs naturally in the petroleum products used as fuel. The susceptibility to poisoning in oxidizing atmospheres is a serious drawback to the use of such catalysts in automobiles. However, small amounts of Pt in the perovskites can significantly improve their poisoning resistance (*12*, *14*). It has been reported that Pt- and Ru-substituted catalysts of the type shown in Fig. 2 are resistant to poisoning by Pb and S (*15*). The mechanism of S poisoning is believed to consist of the oxidation of SO_2 to SO_3 and subsequent reaction of SO_3 with the oxides to form sulfates. This poisoning has been observed under highly oxidizing conditions. It is conceivable that, under the more nearly stoichiometric conditions of the three-way catalysts, oxidation of SO_2 to SO_3 could be prevented. Present designs for noble metal catalyst systems

Table 1. Cations commonly found in perovskite-type oxides. In parentheses is the coordination number, if the radii given are not for 12 coordination; HS and LS refer to high spin and low spin, respectively.

Dodecahedral A site			Octahedral B site		
Ion	Radius (Å)*	Radius (Å)†	Ion	Radius (Å)*	Radius (Å)†
Na^+	1.06	1.32? (IX)	Li^+	0.68	0.74
K^+	1.45	1.60?	Cu^{2+}	0.72	0.73
Rb^+	1.61	1.73	Mg^{2+}	0.66	0.72
Ag^+	1.40	1.30 (VIII)	Zn^{2+}	0.74	0.75
Ca^{2+}	1.08	1.35	Ti^{3+}	0.76	0.67
Sr^{2+}	1.23	1.44	V^{3+}	0.74	0.64
Ba^{2+}	1.46	1.60	Cr^{3+}	0.70	0.62
Pb^{2+}	1.29	1.49	Mn^{3+}	0.66	0.65
La^{3+}	1.22	1.32?	Fe^{3+}	0.64	0.64
Pr^{3+}	1.10	1.14 (VIII)	Co^{3+} (LS)		0.52
Nd^{3+}	1.09	1.12 (VIII)	Co^{3+} (HS)	0.63	0.61
Bi^{3+}	1.07	1.11 (VIII)	Ni^{3+} (LS)		0.56
Ce^{4+}	1.02	0.97 (VIII)	Ni^{3+} (HS)	0.62	0.60
Th^{4+}	1.09	1.04 (VIII)	Rh^{3+}	0.68	0.66
			Ti^{4+}	0.68	0.60
			Mn^{4+}	0.56	0.54
			Ru^{4+}	0.67	0.62
			Pt^{4+}	0.65	0.63
			Nb^{5+}	0.69	0.64
			Ta^{5+}	0.69	0.64
			Mo^{6+}	0.62	0.60
			W^{6+}	0.62	0.60

*From (*47*). †From (*48*).



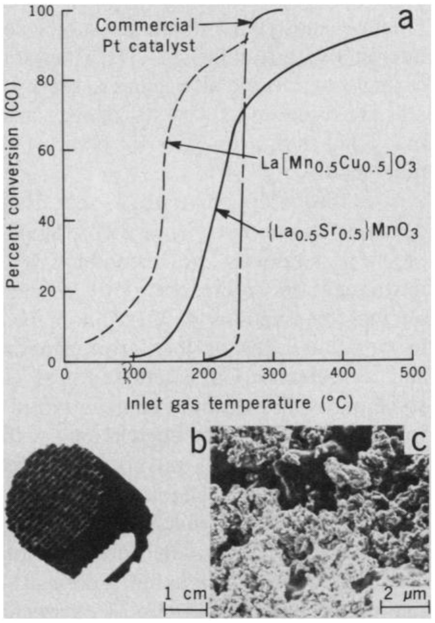


Fig. 2 (left). Application of cobaltate perovskites in the treatment of automotive exhaust from single-cylinder engines. [Adapted from (*15*)] The shading indicates the operating window in the air/fuel ratio for automotive application. (a) The Ru-substituted perovskite $\{La_{0.8}Sr_{0.2}\}[Co_{0.9}Ru_{0.1}]O_3$ supported on a Torvex alumina honeycomb after 1000 hours of exposure to exhaust from gasoline containing 2 grams of Pb per gallon is still effective for the removal of more than 90 percent of the NO in the reducing conditions appropriate for the first bed of a dual-bed catalytic system. The flow of exhaust gas treated in a catalyst volume of 1 liter was 18,000 liter $hour^{-1}$. (b) Cobaltate perovskite substituted with Ru and Pt, $\{La_{0.6}Sr_{0.4}\}[Co_{0.94}Pt_{0.03}Ru_{0.03}]O_3$, on Torvex alumina support after 800 hours of exposure to exhaust from unleaded fuel is effective for the simultaneous removal of HC, CO, and NO_x in the operating "window" of the three-way catalyst system operating at near-stoichiometric conditions. The flow of exhaust gas treated in a catalyst volume of 1 liter was 20,000 liters per hour. Fig. 3 (right). Catalysts supported on cordierite ceramic honeycombs. In the preparation of the perovskite catalysts nitrates were first freeze-dried (*28*, *29*) and then decomposed to oxides and applied to corrugated supports; $\{La_{0.5}Sr_{0.5}\}MnO_3$ and $La[Mn_{0.5}Cu_{0.5}]O_3$ were loaded at the rate of 0.14 and 0.10 gram of perovskite per cubic centimeter of device, respectively. The surface areas of perovskite were 32 and 22 square meters per gram, respectively. (a) Rate of conversion of CO as a function of the temperature of the gas at the inlet of the reactor. (b) The perovskite-covered device. (c) A close-up of the perovskite device in scanning electron microscopy shows the support (smooth area) and the perovskite overlayer (grainy area).

also tend toward more stoichiometric operation to reduce local pollution problems which may be caused by sulfates emitted by automobiles with catalysts.

Advances in the practical application of perovskite catalysts will likely come from empirical studies. It may also be possible to tailor the catalytic properties of these systems on the basis of their known solid-state properties.

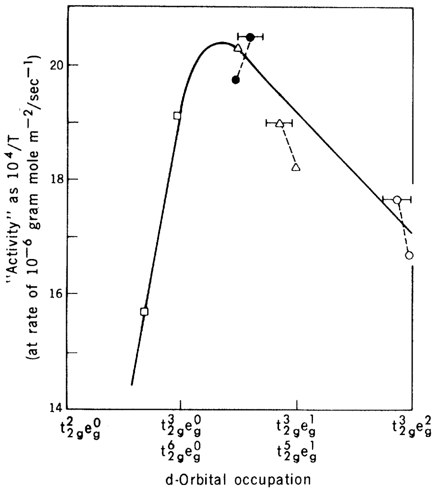


Fig. 4. "Activity" of first-row, transition metal oxide perovskites for the oxidation of CO (*16*). As a measure of the activity, $10^4/T$ is plotted (T is the temperature at which the conversion rate is 10^{-6} gram mole per second per square meter of surface area in a 2 : 1 mixture of CO and O_2 at atmospheric pressure). The activities of chromates (□), manganates (△), ferrates (○), and cobaltates (●) are plotted at the appropriate *d*-orbital occupation corresponding to the average valence of the transition metal ion.

Catalysis and the Solid State

A knowledge of the relation between the catalytic and solid-state properties of inorganic compounds is essential for the systematic (rather than empirical) design and tailoring of efficient catalysts. In the pursuit of these relations, the availability of a large class of isostructural compounds characterized by flexibility and adaptability is a great benefit (*5, 30*). The structure and composition of the ABO_3 perovskites simplify the formidable task of sorting out the needed correlations: the A ions are in general catalytically inactive, and the active transition metal ions at the B position are placed at sufficiently large distances from each other (about 4 angstroms) that a gas molecule interacts with a single site (*31*). Even for a single active metal B center, there is still the freedom to vary its valence and many physical properties by choices of the "modifying" A ion.

It is probably naive to expect that catalysis can be correlated with a single physical parameter, be it conductivity, magnetization, or ferroelectricity. Experimental observations (*6, 32*) of anomalies in catalytic rates at the ferromagnetic and ferroelectric Curie temperatures of some perovskites cannot be generalized. In fact, the search for correlations with solid-state parameters must be guided by fairly detailed knowledge of the mechanism of the catalytic reaction selected to test the correlation. The test reaction chosen should be simple but representative of the particular group of chemical conversions of interest (oxidation reactions, hydrogenations, or whatever). What kinds of correlations may be expected? Thermodynamic parameters, such as the enthalpy of formation of oxygen vacancies, are appropriate to correlate with intrafacial catalytic processes, in which by definition (*33*) the catalyst enters as a reagent that is partly consumed and regenerated in a continuous cycle. Many selective oxidation processes in industry, such as the formation of butadiene from butene or the production of acrylonitrile from propylene and NH_3, belong to this class (*3*). In these oxidations, oxygen from the oxide catalyst is consumed and replenished continuously. A correlation with electronic parameters of the solid is more appropriate in suprafacial catalytic processes (*33*), in which the surface serves as a template providing electronic orbitals of the proper energy and symmetry for the bonding of reagents and intermediates.

An example of an intrafacial process is the reduction of NO, which occurs through dissociative chemisorption on an O vacancy (V_0) on many cobaltate and manganate perovskite catalysts (*13, 23, 33, 34*)

$$NO + [M–V_0–M] \rightarrow N_{ads} + [M–O–M]$$

In this reaction, the reduced and oxidized surfaces are symbolized by [M–V_0–M] and [M–O–M], respectively. The valence of the metal M is increased by this reaction; N_{ads}, the resulting N fragment, which probably has to be stabilized by interaction with other adsorbates, may react further to form N_2, N_2O, and so forth. The V_0 is restored by a reducing agent in the gas, for example,

$$H_2 + [M–O–M] \rightarrow H_2O + [M–V_0–M]$$

It is understandable from the mechanism that the number of V_0 in the surface is important for the rate of conversion of NO. In the perovskite systems based on $LaMnO_3$, we have a means of systematically varying the relevant solid-state parameter, the bond energy E(O) for oxygen in the surface. For the (100) perovskite surface with composition BO_2 (Fig. 1), E(O) is determined by the sum of the energies of two B–O bonds in the first layer and of two A–O bonds to the second layer. If the identity of the BO_2 layer is maintained, E(O) can be modified through the A–O bonds by substitutions in the A sites. The most drastic modification is the introduction of a cation vacancy ϕ on the A site. The presence of such vacancies and of a complete oxygen sublattice in the compound $La_{0.9}\phi_{0.1}MnO_3$ has been demonstrated by x-ray and neutron diffraction studies (*35*). Because of the lower E(O), this compound is a much more active catalyst than $LaMnO_3$ for the conversion of NO (*34*). In manganate perovskites $(A,A')MnO_3$ with A site substitutions adjusted to vary E(O) while maintaining the same average Mn valence state (and the same electrical conductivity), the catalytic activity increased as the value of E(O) decreased for combinations of A and A′ in the sequence (La,Sr), (La,K), (La,ϕ), and (Bi,K) (*36*).

The oxidations of CO with O_2 over perovskite-type catalysts at temperatures between 100° and 300°C have been suggested as examples of suprafacial catalysis (*33*). This suggestion was supported by extensive work on the system $(La,A')CoO_3$, where A′ was chosen to vary the valence of Co—by charge compensation—between Co^{2+} and Co^{4+} when A′ is Ce^{4+} or Sr^{2+}, respectively. Introduction of Co^{2+} led to an increase in catalytic activity, and introduction of Co^{4+} to a decrease (*26*). The valence states of Cr in $LaCrO_3$ and of Mn in $LaMnO_3$ were similarly changed by the introduction of A site substituents that were shown (*5*) to lead to charge compensation (*26, 33*). Variations in the valence states were also brought about by partial reduction, within the homogeneity ranges of the perovskite systems. In the oxidation of CO over this series of perovskites, the catalytic activity was correlated with the occupation of the 3*d* levels in the surface (Fig. 4). For optimum activity the d_{z^2} level, the lowest e_g level in the truncated octahedral crystal field of surface ions, has to be occupied by less than one electron, whereas the t_{2g} levels below the d_{z^2} level must be filled. This correlation can be understood in connection with the kinetic data (*26*) which show that the binding of CO to the surface is a critical part of the process, since the reaction rate varies as the partial pressure of CO, $p_{CO}{}^n$, where $0.3 < n < 0.9$. In the Chatt-Dewar model for the binding of CO as a carbonyl to transition metals, binding is optimal when donation of the carbon lone pair into the d_{z^2} metal orbital and simultaneous back-bonding of t_{2g} electrons to the antibonding π^* orbital of CO are possible (*37*). The correlation of the rate with the occupation of 3*d* orbitals is therefore consistent with the kinetic data and a mechanistic view based on the Chatt-Dewar model. However, independent measurements of the adsorbed species are necessary for the formulation of a detailed mechanism.

It is to be expected that further experimental correlations of catalytic activity and solid-state parameters will be developed. The perovskites offer a wide scope for such work. They are also useful as relatively simple and well-studied model systems in theoretical work. Surface states and mechanistic pathways for chemical conversions at the surface are currently being explored, for example, in $SrTiO_3$ (*38*).

Preparation and Characterization

Since catalysis occurs at surfaces, only the exterior layers of atoms play a significant role. The remainder of the material is "wasted" in a catalytic sense except as a suitable support for the exterior layers. Catalysts are therefore prepared with the maximum surface-to-volume ratio consistent with low cost of preparation, ease of handling, and stability toward particle growth at the temperature of use. As an illustration, a cube of catalyst with a volume of 1 cubic centimeter has a surface area of 6 cm^2; divided into cubes 1 micrometer on an edge it has a surface area of 6×10^4 cm^2 and into cubes 100 Å on an edge it has a surface area of 6×10^6 cm^2 or 600 m^2. Although average particle sizes of 1 μm are easily attainable, specialized preparative techniques are needed for those of 100 Å or less. In ceramic processing, the preparation of oxides with high surface area has long been a major goal, because such materials are needed for the production of dense sintered bodies with fine grains. This microstructure is often necessary in applications of the mechanical, magnetic, or electrical properties of ceramics. Not surprisingly, many of the special techniques developed with this goal in mind are directly applicable to the preparation of perovskite catalysts.

However, there is an important difference. In ceramics the usual goal is a dense sintered body with a very low surface area, and, in fact, the surface free energy of the powder is the driving force for densification. In catalysts the goal is to prevent sintering and to maintain the high surface area necessary for commercial effectiveness. The loss of surface area due to sintering can be minimized in several ways. The simplest approach is to prepare a catalyst that is sufficiently active at low temperatures, so that sintering is not a problem. Alternatively, the crystal chemistry may be controlled to ensure low diffusion rates of the ions. Information on the effect during use of the partial pressure of oxygen on the oxygen stoichiometry, vacancy concentration, and cation oxidation states is seldom available. However, empirical evidence demonstrates the advantages of some perovskite compositions over others. Perovskites with the composition $La_{1-x}Sr_xMnO_3$ ($0 < x < 0.5$) can be easily synthesized with a high surface area and are resistant to loss of surface area by sintering (*28*). Perovskite cobaltates with noble metal substitutions were also reported to be resistant to deactivation by sintering at 900°C (*15*). Segregation of inactive binary oxides at the surface of the catalyst is similarly associated with diffusion. Deleterious effects were demonstrated for $La_{0.7}Pb_{0.3}MnO_3$, a perovskite catalyst that is easily deactivated at temperatures as low as 400°C (*13*), both by loss of surface area and by the migration of Pb compounds to form an inactive layer at the surface (*39*).

Table 2. Comparison of preparative techniques for perovskites.

Technique	Advantages	Disadvantages	Range of surface areas (m^2/g)
Mixed oxide	Simple, no specialized equipment, wide range of composition	Low surface area, difficult to achieve chemical homogeneity	< 2
Freeze-drying	Very good chemical homogeneity, high surface area	Needs mutually soluble compounds, two-step drying process (freeze and freeze-dry), specialized equipment	10 to 30
Spray-drying	Good chemical homogeneity, high surface area, single-step drying process	Needs mutually soluble compounds, highly specialized equipment	10 to 20
Precipitation	Uses simple laboratory equipment	Needs mutually soluble compounds with common precipitating agent	1 to 10

Synthesizing perovskites is an easy task because such a large array of ions can be used (Table 1). The simplest method is often by mixing the constituent oxides or their carbonates. But, because these reagents have relatively large particles and are poorly mixed on a microscopic scale, a chemically homogeneous compound is often produced only at relatively high temperatures. This results in a product with large particles and low surface areas, typically 1 to 2 square meters per gram. Nevertheless, the technique is very versatile and is often used for catalytic studies when a high surface area is not necessary. A large number of rare-earth manganate perovskites have been prepared by this method (*40*). Homogeneous perovskite catalysts with higher surface areas may be made by solution techniques. During removal of the solvent and decomposition of the remaining salts to oxides, it is necessary to preserve the chemical homogeneity which was present in the liquid solution as much as possible. This allows final synthesis of the perovskite at low temperatures, resulting in high surface areas. A variety of perovskite catalysts has been prepared from nitrate solutions by freeze-drying (*41*), spray-drying (*42*), and precipitation (*43*). Table 2 compares these methods of preparation with the mixed oxide technique.

The perovskite catalysts are generally used on relatively inert ceramic supports. This hinders sintering by dispersing the catalytic material while at the same time minimizing the amount of catalyst needed by providing for the ready access of gaseous reactants to the surface. One may prepare the device by dipping the support into a slurry of the perovskite powder, drying, and firing to bind the powder to the support. To improve the bond, other inert powders such as very fine hydrated aluminum oxide are sometimes added to the slurry. This procedure may also improve the rheology of the suspension. Alternatively, the perovskite may be synthesized directly on the support; in this case the support is impregnated with a solution of the appropriate cations, then dried, and fired. The process is similar to that used for Pt catalysts.

The initial characterization of perovskite catalysts includes a determination of the compositional analysis, the crystal structure, and the surface area. For detailed characterization, it is desirable to define the valence states and lattice positions of the cations. A study of the perovskite $\{La_{0.7}Pb_{0.3}\}MnO_3$ doped with various amounts of Pt serves as an example (*44*). As stated above, noble metals in perovskites can play an important role, particularly with respect to resistance to S poisoning. However, prior to the study of Johnson *et al.*, the oxidation state of Pt in perovskites was not known. These investigators used ESCA (electron spectroscopy for chemical analysis, in which electron emission is stimulated by x-rays incident on the sample) to determine the oxidation state of Pt in $\{La_{0.7}Pb_{0.3}\}MnO_3$ prepared under a variety of conditions. These results (Fig. 5) show that in single crystals and in polycrystalline samples inpregnated with Pt and fired at 700°C in O_2 the Pt at the surface is primarily in the tetravalent state. Metallic Pt was predominant in polycrystalline samples impregnated with Pt and reduced in H_2 at 400°C.

One usually measures the catalytic activity by passing the reactant gases over the perovskite at controlled temperatures and analyzing the exit gases for the desired products or unreacted gases. Gas chromatography, mass spectroscopy, nondispersive infrared analysis, and flame-ionization analysis have been used. In initial evaluation it is customary to use synthetic gas mixtures. For evaluations of perovskite catalysts that are more representative of automotive use, internal combustion engines are used (*15, 25*).

A simple and rapid technique for comparing the activities of small amounts of perovskite catalysts is differential thermal analysis (*45, 46*). A small amount of catalyst is placed in contact with one junction of a differential thermocouple, and a catalytically inert material is placed in contact with the other junction. The reactant gas is passed over the catalyst while the temperature is increased. As the reactants are oxidized, the heat generated by the oxidation is sensed by the differential thermocouple and the magnitude of this output is proportional to the activity. This technique can be made semiquantitative (*46*), but it is of value primarily for the rapid screening of catalysts.

Summary

In a time of growing need for catalysts, perovskites have been rediscovered as a family of catalysts of such great diversity that a broad spectrum of scientific disciplines have been brought to bear in their study and application. Because of the wide range of ions and valences which this simple structure can accommodate, the perovskites lend themselves to chemical tailoring. It is relatively simple to synthesize perovskites because of the flexibility of the structure to diverse chemistry. Many of the techniques of ceramic powder preparation are applicable to perovskite catalysts. In their own right, they are therefore of interest as a model system for the correlation of solid-state parameters and catalytic mechanisms. Such correlations have recently been found between the rate and selectivity of oxidation-reduction reactions and the thermodynamic and electronic parameters of the solid.

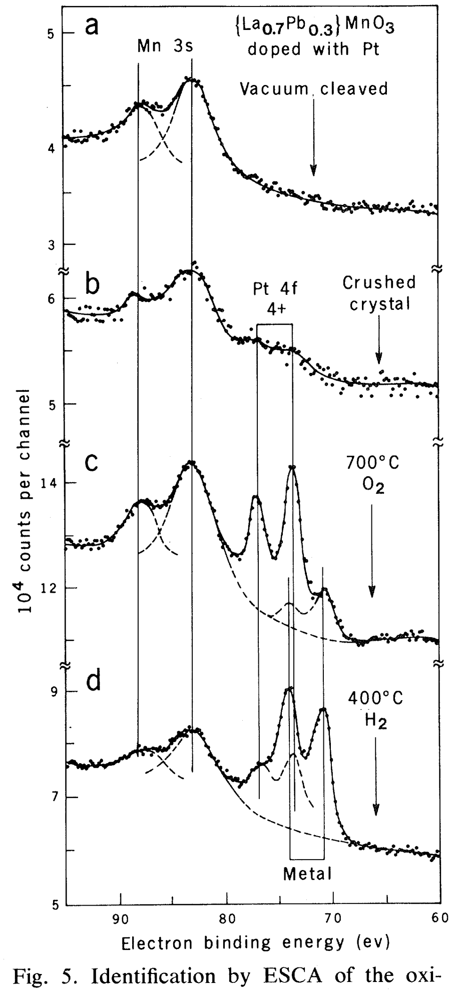


Fig. 5. Identification by ESCA of the oxidation state of Pt in the perovskite $\{La_{0.7}Pb_{0.3}\}MnO_3$ doped with Pt (*44*). The illustrated energy spectrum encompasses the Mn 3*s* and Pt 4*f* electrons. The oxidation state is identified by the shift in binding energy of the Pt 4*f* electrons. (a) A vacuum-cleaved single crystal containing an insignificant amount of Pt. (b) A crushed crystal containing about 5200 parts per million of Pt which is shown to be tetravalent. (c) A polycrystalline material with 5500 parts per million of Pt added from a chloroplatinic acid solution, reduced and heat-treated at 700°C in O_2; this treatment results in a heavy concentration of tetravalent Pt near the surface with a detectable amount of metallic Pt. (d) Same as in (c) but with a reduction of chloroplatinic acid in H_2 at 400°C, resulting in largely metallic Pt.

For commercial processes such as those mentioned in the introduction, perovskite catalysts have not yet proven to be practical. Much of the initial interest in these catalysts related to their use in automobile exhaust control. Current interest in this field centers on noble metal-substituted perovskites resistant to S poisoning for single-bed, dual-bed, and three-way catalyst configurations. The formulations commercially tested to date have shown considerable promise, but long-term stability has not yet been achieved.

A very large fraction of the elements that make up presently used commercial catalysts can be incorporated in the structure of perovskite oxides. Conversely, it is anticipated that perovskite oxides, appropriately formulated, will show catalytic activity for a large variety of chemical conversions. Even though this expectation is by no means a prediction of commercial success in the face of competition by existing catalyst systems, it makes these oxides attractive models in the study of catalytic chemical conversion. By appropriate formulation many desirable properties can be tailored, including the valence state of transition metal ions, the binding energy and diffusion of O in the lattice, the distance between active sites, and the magnetic and conductive properties of the solid.

Only a very small fraction of possible perovskite formulations have been explored as catalysts. It is expected that further investigation will greatly expand the scope of perovskite catalysis, extend the understanding of solid-state parameters in catalysis, and contribute to the development of practical catalytic processes.

References and Notes

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49. We thank our many colleagues at Bell Laboratories who have contributed to the study of perovskite catalysts, in particular, L. E. Trimble, E. M. Vogel, A. Cooper, and F. Schrey.