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The Nature and Effects of Platinum in Perovskite Catalysts

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It has been observed that the catalytic activity of $La_{0.7}Pb_{0.3}MnO_3$ for CO oxidation is greatly enhanced by the addition of platinum. The enhancement is up to 100 times greater than that expected for homogeneously distributed Pt whose specific activity is that of metallic Pt on Al_2O_3. X-Ray photoemission spectroscopy (ESCA) experiments show that Pt in these perovskites is in the form of the dissolved tetravalent ion. Catalytic activity measurements on $BaPtO_3$ show that the specific activity of Pt^{4+} in that structure is about twice that of metallic Pt on Al_2O_3. Various observations of Pt concentrating at the surfaces of $La_{0.7}Pb_{0.3}MnO_3$ can, in part, account for the enhanced activity. However, Pt^{4+} dispersed in $La_{0.7}Pb_{0.3}MnO_3$ may still have a higher activity than Pt^{4+} in $BaPtO_3$ since the measured surface concentration of Pt^{4+} cannot completely account for the observed activity. Additions of Pt to supported $La_{0.5}Sr_{0.5}MnO_3$ and $LaMn_{0.5}Cu_{0.5}O_3$ affect the activity of the former only slightly and may degrade the activity of the latter for CO oxidation. On the other hand, the Pt renders both compounds resistant to SO_2 poisoning, the more so for the $La_{0.5}Sr_{0.5}MnO_3$.

INTRODUCTION

Several recent studies (*1–4*) have recognized that Pt in perovskite catalysts plays an important role in imparting resistance to poisoning by SO_2. It has also been suggested that Pt can, in some cases, contribute significantly to the catalytic activity observed for the oxidation of CO.

Yao (*1*) reported on lead borate flux grown single crystals of $La_{0.7}Pb_{0.3}MnO_3$ containing 30 ppm Pt and on a similar composition prepared by precipitation but without Pt. The specific activity of the monocrystalline material is somewhat higher than that of precipitated material for CO oxidation and considerably higher for hydrocarbon oxidation. Using the data reported by Yao (*1*) for CO oxidation over these manganates and the average value reported for metallic Pt, calculations were made to find if the increased activity observed in the monocrystals was consistent with that expected from the metallic Pt. The surface area of a Pt atom was taken as 11 Å^2 (*5*). These calculations showed that the Pt cannot account for the observed enhancement of activity unless it is concentrated at the surface or unless the activity of Pt in these structures is greater than that for metallic Pt. Because of the higher activation energy used for the Pt the magnitude of this discrepancy decreased with increasing temperatures. At 200°C the calculations predict that the concentration of Pt at the surface is over 300 times as great as that predicted for the bulk (or that homogeneously distributed Pt is over 300 times more active per atom than metallic Pt) while at 400°C the factor is 8.

Yao (*1*) also reported a further increase in the activity of the monocrystalline perovskite samples when SO_2 was added to the reaction system, whereas the copre-

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cipitated perovskite without Pt was irreversibly poisoned. The increase in activity was as large as a factor of 8 and occurred at temperatures greater than 400°C. It should be kept in mind that metallic Pt usually shows a small decrease in activity when SO_2 is introduced into the reaction system. An activity increase with SO_2 has also been reported by Johnson *et al.* (*6*) for $La_{0.5}Pb_{0.5}MnO_3$ with Pt added at the 200–1000 ppm level.

Katz *et al.* (*4*) have also investigated the perovskite composition $La_{0.7}Pb_{0.3}MnO_3$ prepared as single crystals in Pt crucibles and as polycrystalline powders from hydroxide precipitation. The Pt content of the single crystals was measured as 200–300 ppm. They also observed the enhanced activity of the Pt containing material and calculated that the Pt, if homogeneously distributed, must have a specific activity 10^2–10^3 times higher than that observed for metallic Pt on Al_2O_3. Again, the Pt containing perovskite showed superior resistance to SO_2 poisoning compared to other base metal oxides.

Gallagher *et al.* (*2*), working with Pt-free, flux grown single crystals of $La_{0.7}Pb_{0.3}MnO_3$ (grown by a cold wall crucible technique) (*7*) have shown that their specific activity is similar to that of Pt-free polycrystalline (La, Pb)MnO_3 prepared by several other techniques. It was also shown that for CO oxidation the activity due to Pt in samples with 570 ppm Pt or less is small compared to the "intrinsic" (freshly prepared surfaces) activity of $La_{0.7}Pb_{0.3}MnO_3$, but is significant for concentrations in the 1600–5500 ppm range.

Gallagher *et al.* (*3*) have also reported that Pt-free single crystals (*7*) are poisoned by SO_2 but samples with as little as 200 ppm Pt showed appreciable resistance to poisoning by SO_2.

Recent reports (*8*, *9*) of the use of noble metals in perovskites illustrate the possible technological significance of these materials for automotive exhaust emission control. Perovskites with Pt and Pd substituted in the "B" site are reported to show good thermal stability and are resistant to high concentrations of lead, phosphorus, and sulfur. This is particularly significant since nobel metal catalysts are usually poisoned by lead and base metal oxide catalysts are usually poisoned by sulfur. However, relatively high concentrations of noble metals were used in these studies.

While there is ample evidence of a high activity of Pt in (La, Pb)MnO_3, until recently no direct evidence has been presented concerning the oxidation state of Pt in these materials. Most importantly, it has not been clear whether the Pt is in the form of small metallic particles or as ionic Pt dissolved in the crystalline structure.

Croat *et al.* (*10*, *11*) have recently examined $La_{0.7}Pb_{0.3}MnO_3$ crystals incorporating Pt and have reported X-ray photoelectron spectroscopy data (XPS or ESCA) on the Pt. They found a 100-fold increase in the concentration of Pt at the surface compared with the bulk values and conclude that this surface concentration explains adequately the activity enhancement observed for samples with Pt. They (*10*, *11*) also reported that chemical shift data on Pt indicate a "heavily oxidized" Pt surface layer which is reduced to nearly a metallic state with heavy etchings in HNO_3.

X-Ray photoemission spectroscopy (ESCA) provides a sensitive technique for the determination of the valence state of many elements, even when dissolved in low concentration in solids. In the case of platinum the $4f$ electrons offer the most sensitive indication because they are the sharpest lines and they have the largest photoelectric cross section at ESCA energies. In $La_{1-x}Pb_xMnO_3$ these lines are well separated from those of the other constituents.

The purpose of this study was to determine the oxidation state of Pt in perovskite crystals and attempt to compare the specific activity of this Pt with that of metallic Pt. We have also sought to generate additional data on the role of Pt with respect to catalytic activity and SO_2 poisoning resistance in perovskite compounds other than $La_{0.7}Pb_{0.3}MnO_3$.

METHODS

Crushed crystalline $La_{0.7}Pb_{0.3}MnO_3$ specimens (provided by J. P. Remeika) were prepared from a lead borate flux as described earlier (*12*). From various lots, a fraction of <44 μm fines were chosen because of the high Pt content (5200 ppm). This sample lot along with others had been used in earlier studies (*2*, *3*). Polycrystalline samples of $La_{0.7}Pb_{0.3}MnO_3$ were prepared by mixing appropriate ratios of La_2O_3, PbO and Mn_2O_3; and firing at 1000°C for 16 hr in air. Part of this sample lot was doped with 5500 ppm Pt by adding sufficient H_2PtCl_6 dissolved in water and mixing until dry. This was reduced at 400°C for 2 hr in 6.6% H_2 in N_2 and then refired at 700°C for 16 hr in O_2 in an attempt to diffuse the Pt into the perovskite structure.

$La_{0.5}Sr_{0.5}MnO_3$ and $LaCu_{0.5}Mn_{0.5}O_3$ were prepared by freeze-drying nitrate solutions as described earlier (*13*). The dried nitrates were calcined in a rotating fused silica drum by heating to 500°C at 50°C/hr and holding for 2 hr at 500°C in a vacuum of about 1 torr. Subsequent heat treatment was done at 700°C for 2 hr in O_2. These powders were supported on 1 in. long by 1 in. diam pieces of corrugated corderite monoliths (3M AlSiMag 795, split cell, stacked 8 cells/in, 0.008 in. wall) by dipping the ceramic supports into a water slurry of the catalyst and firing at 500°C. This was repeated until about 1.1–1.7 g of catalyst were on the support. A final heat treatment was done at 700°C in O_2 for 2 hr.

Controlled amounts of Pt were added to these fabricated supports by dipping them into solutions of H_2PtCl_6 of varying concentrations. The solution laden supports were dried, reduced at 500°C for 4 hr in 6.6% H_2 in N_2 and then fired at 700°C for 16 hr in an atmosphere of 2% CO, 2% O_2, 96% N_2. Total surface area of catalyst on these devices ranged from 26 to 30 m^2 for $La_{0.5}Sr_{0.5}MnO_3$ and 9 to 18 m^2 for $LaMn_{0.5}Cu_{0.5}O_3$. Pt contents were determined using quantitative atomic absorption spectroscopy.

Samples of metallic Pt on Al_2O_3 with similar Pt loadings were also prepared on similar supports with an Al_2O_3 "wash coat" using the solution uptake method described for the supported perovskite catalysts.

$BaPtO_3$ was prepared by two methods as described in another report (*14*). In brief, one method involved reacting BaO_2 and PtO_2 in a sealed capsule at 1000°C for 2 hr at 28,000 psi external pressure, and the other method involved calcining a precipitated $BaPt(OH)_6$ at 600–700°C in O_2 at ambient pressure.

ESCA data were taken with a Hewlett-Packard 5950A spectrometer operating with monochromatized AlKα radiation, 1486.6 eV. The samples were of three kinds: single crystal with <100 ppm Pt, crushed crystal with 5200 ppm Pt as described earlier and sintered powder with 5500 ppm Pt as described earlier. The single crystal was cleaved in the machine under vacuum and run without exposure to air. The others were pressed into a thin layer of conducting epoxy. After the epoxy had been set, the excess powder was shaken off. The samples were run without additional surface treatment.

The catalytic activity of the powdered $La_{0.7}Pb_{0.3}MnO_3$, Pt on Al_2O_3 (0.5% Pt, Englehard Industries), and $BaPtO_3$, all of known surface area, was measured in a small reactor (*2*) containing sufficient catalyst mixed with 44–88 μm Al_2O_3 to give 0.2 m^2 of catalyst surface. Temperature was controlled at a heating and cooling rate of 2°C/min using an external gas

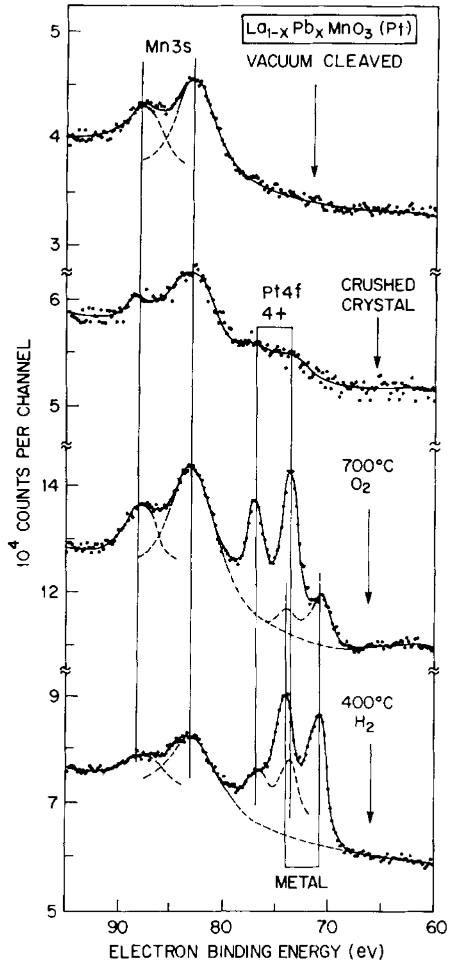

FIG. 1. X-ray photoemission spectra of various samples of $La_{1-x}Pb_xMnO_3$(Pt). (a) A vacuum-cleaved single crystal with < 100 ppm Pt, (b) crushed single crystals with 5200 ppm Pt, (c) sintered material with 5500 ppm Pt annealed at 700°C, and (d) the same sintered material annealed in hydrogen at 400°C.

fluidized sand bath. A CO oxidation test reaction was used with 1% CO, 1% O_2 in N_2 flowing at 400 cm^3/min. Gas analyses were made by gas chromatography. The temperature was monitored by a thermocouple inserted in the bed. No corrections were made for partial pressure effects and any quantitative activity data should be derived from the measurements at low conversions.

Activity of the supported samples was measured in a reactor described previously (*15*) again using CO oxidation as a test reaction. In short, preheated gas (2% CO, 2% O_2 in N_2) was passed over the support at a rate of 24,000 h^{-1} GHSV (gaseous hourly space velocity calculated for a volume of 1 in. diam by 1 in. long at STP). Analysis was by gas chromatography. The heating and cooling rates were 3°C/min. The temperature of the inlet gas and the gas about $\frac{3}{4}$ in. into the support was monitored. The inlet temperatures are reported. It is recognized that both radial and longitudinal temperature gradients exist in this type of reactor but it does serve to simulate conditions which might be found in an application such as auto exhaust control.

Phase identification was done by X-ray diffraction. Surface areas were measured by the BET technique using adsorption of N_2 or Kr. Pt surface areas were measured by H_2 chemisorption using the method of Adams *et al.* (*5*). Pt analyses in single crystalline (La, Pb)MnO_3 were done by quantitative emission spectroscopy.

RESULTS AND DISCUSSION

Oxidation State of Pt in $La_{0.7}Pb_{0.3}MnO_3$

The X-ray photoemission (ESCA) lines of all elements present in the $La_{0.7}Pb_{0.3}MnO_3$ samples were monitored, but the most useful information was obtained in the 35 eV interval in Fig. 1 which contains the Mn 3*s* and Pt 4*f* lines. This interval is bracketed by a weak Mn 3*p* line at 48 eV and the strong La 4*d* line at 102 eV. The Pb $5p_{\frac{3}{2}}$ which falls under the Mn 3*s* doublet is sufficiently broad and weak not to distort the Mn spectrum seriously. The two sets of features which appear in this interval both consist of doublets. The Mn 3*s* multiplet splitting is due in essence to 3*s*–3*d* exchange and in principle provides an indication of the valence state of the manganese. The multiplet splittings for Mn_2O_3 and MnO_2 are, respectively, 5.5 and

4.6 eV (*16*). The vertical lines through the Mn 3*s* region are about 5 eV apart. Because of the large natural linewidth it is not possible to determine the oxidation state of Mn or to confirm the coexistence of two different oxidation states.

The narrower platinum lines provide much more definitive information. The 4*f* spectrum of a single valence state of Pt is a doublet with 3.3 eV separation due to the spin–orbit interaction. Except for small effects due to differences in photoelectric cross section the intensity ratio is 3:4. Comparison of the data for the largely Pt-free, vacuum cleaved crystal with those for the sintered materials containing 5500 ppm Pt clearly identifies the Pt lines. However, it is also evident that there is in each case a superposition of *two* doublets with the same positions but quite different intensities. The doublet separation is about 3 eV, with the lower energy one having its strong line near 71 eV. This binding energy identifies the Pt as metallic, literature values falling near 71.2 eV. (The data shown were obtained with the sample flooded with thermal electrons to avoid charging of the surface. Data taken without this precaution were slightly shifted toward greater binding energy and somewhat less well resolved, indicating differential charging.) The crushed crystal with nominally the same Pt concentration as the sintered powder has much weaker Pt lines in the positions of the doublet with greater binding energy. This is a good indication that the Pt in the sintered material is not uniformly distributed throughout the bulk.

Fuller interpretation of the results depends on a calibration of the shift in binding energy for the various oxidation states of platinum in oxygen coordination. We here depend on the work of Bancroft *et al.* (*17*) who give binding energies of 71.3, 72.4, and 74.2 for metallic platinum, PtO and PtO_2, respectively. The Pt position agrees well with our own measurements on bulk metallic Pt (not shown in Fig. 1).

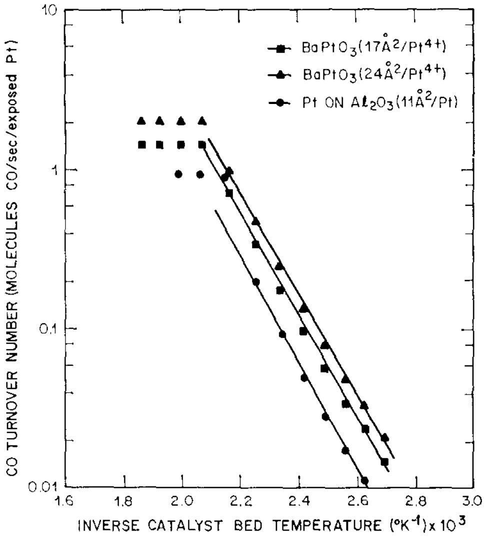

FIG. 2. Specific activity of Pt in metallic and ionic states. (Parentheses refer to assumed average area per Pt.)

The most immediately useful information is the Pt to PtO_2 shift of 2.9 eV. This agrees well with the separation of the two doublets found in the present experiments and serves to identify them as due to Pt^{4+} and metallic Pt. The latter may well reside on the surface. If this conjecture is correct the measurements will tend to overestimate the amount of metallic Pt because of the limited escape depth of electrons from the dissolved Pt^{4+}. In the case of the hydrogen sintered material the separation of the two doublets appears to be a little smaller but it still favors Pt over Pt^{2+} for the doublet with smaller binding energy.

These measurements thus give clear evidence for the presence of quadrivalent platinum in both sintered and crystalline (La, Pb)MnO_3 doped with Pt.

Hydrogen chemisorption measurements were made on these samples of $La_{0.7}Pb_{0.3}MnO_3$. On the crushed single crystalline sample virtually no chemisorption of H_2 was detected. The absence of metallic Pt is consistent with the ESCA data in Fig. 1. On the doped polycrystalline sample first reduced and then oxidized at 700°C about

9% of the total observed surface adsorbed H_2 (0.085 m^2/g of Pt by chemisorption and 0.92 m^2/g total surface area by BET). Thus about 4.5% of the total Pt was accounted for as exposed metal (a 1 g sample at 5500 ppm Pt has 0.0055 g Pt and at 0.085 m^2 Pt/g, 0.00025 g Pt are exposed). If this is in the form of metal crystallites with 30% of the Pt atoms in a crystallite exposed at its surface then about 15% of the Pt would be accounted for as metallic. If no other unexposed metallic Pt exists then by difference 85% of the Pt is ionic (does not chemisorb H_2). This too is qualitatively consistent with the results of the ESCA study in Fig. 1. For the sample doped with Pt and reduced at 400°C in H_2, no appreciable chemisorption was observed despite the ESCA results showing largely metallic Pt near the surface. However, during the subsequent oxidations of this specimen lot it was noted that chlorides were evolved indicating residual chlorides from the chloroplatinic acid and the presence of these could have contaminated the metal surfaces for the chemisorption of H_2. (Other samples have been prepared with chloroplatinic acid in which the reduction was carried out at 500°C. For these, metallic Pt is measurable by chemisorption and residual chlorides have not been observed after subsequent heat treatments.)

Because the preparative technique for the polycrystalline samples induces a relatively heavy Pt coating on the particles, and because metallic Pt was observed by ESCA after the initial reduction of these samples, the possibility existed that the Pt^{4+} observed by ESCA on the oxidized samples may be due to a layer of PtO_2 rather than Pt^{4+} dissolved in the perovskite. X-Ray diffraction and selected area electron diffraction failed to show measurable amounts of PtO_2. Also, bulk Pt which was heat treated in O_2 at 700°C showed no evidence of PtO_2 using ESCA. Therefore, the Pt^{4+} observed on the $La_{0.7}Pb_{0.3}MnO_3$ is that of dissolved ions. The size of the Pt^{4+} ion certainly suggests that it resides on the "B" site of the perovskite lattice.

Activity of Pt^{4+} in $BaPtO_3$

In order to measure the activity of Pt^{4+} in a system similar to these perovskites, $BaPtO_3$ was synthesized and characterized (*14*). The ESCA results of that study show only Pt^{4+} with no evidence of metallic Pt. The structure is not completely defined but it is believed to be a hexagonal layered perovskite type structure somewhat similar to $BaRuO_3$ (*18*). While the structures of these two compounds are not isomorphous, it is felt that since the ionic radii of Ru^{4+} and Pt^{4+} are nearly identical the packing density of Pt^{4+} in $BaPtO_3$ is probably close to that of Ru^{4+} in $BaRuO_3$. In earlier calculations on perovskite, it was assumed that the crystallites exposed the (100) faces of the ideal cubic structure. This assumption gave the maximum concentration of B site per unit surface area. A cubic cell having $\frac{1}{9}$ the volume of the reported $BaRuO_3$ cell (*18*) would correspond to an exposure of 17 Å/Pt^{4+} ion. More realistically an average cleavage might be represented by the hexagonal (110) plane. This represents 24 $Å^2/Pt^{4+}$ ion.

Specific activity data (CO turnover rate in molecules of CO oxidized per exposed Pt per sec) taken using the powder reactor are shown in Fig. 2 for Pt metal using 11 $Å^2$/Pt atom (*5*) and for the $BaPtO_3$ using both of the above assumptions (17 and 24 $Å^2/Pt^{4+}$) for the surface density of Pt ions. The data for the metallic Pt agree well with that reported by Katz *et al.* (*4*). Most important for this study is the similarity between the metallic and ionic Pt. They both have similar slope indicating similar apparent activation energies, but the ionic Pt is about twice as active as the metallic Pt.

This factor of two is, of course, insufficient to explain the observed activity enhancement in Pt doped (La, Pb)MnO_3. On the other hand, this observed activity for Pt^{4+} in $BaPtO_3$ may not be representative of that for (widely dispersed) Pt^{4+} in (La, Pb)MnO_3. Bockris and McHardy (*19*) have observed large increases in the rate of oxygen reduction by electrocatalysis in sodium tungsten bronze when traces of Pt were present. The increased activity for reduction was $>10^3$ times larger than that predicted for metallic Pt in these materials. This anomaly was attributed to a synergistic model for Pt inclusions in the sodium tungstate bronze. Furthermore, in structures having hexagonally close packed BaO_3 layers such as $BaNiO_3$ and $BaRuO_3$ the face shared octahedra of NiO_6 or RuO_6 bring the metal atoms very close [closer in $BaRuO_3$ than in metallic Ru (*18*)] and this suggests metallic bonding. If this is the case for $BaPtO_3$, then the activity of Pt^{4+} dispersed in the "B" sites of corner shared octahedra in $La_{0.7}Pb_{0.7}MnO_3$ may be greater than that observed in $BaPtO_3$.

Activity of Pt^{4+} in Crushed Crystalline $La_{0.7}Pb_{0.3}MnO_3$

The activity of crushed single crystalline $La_{0.7}Pb_{0.3}MnO_3$ used in the ESCA study (5200 ppm Pt) and of a Pt-free crushed single crystalline sample grown from a flux in a cold walled crucible (*7*) are shown in Fig. 3. These data were taken using the powder reactor on samples with nearly equivalent surface areas. In each case the data represent the initial cycle of fresh samples in the reactor before any deactivation due to Pb migration at higher temperatures (*2*, *15*) had taken place. Using the activity of Pt^{4+} assuming the (110) face in Fig. 2 (24 Å^2/Pt^{4+}) a surface enhancement of 70-fold in Pt^{4+} over the bulk concentration is necessary to account for the enhanced activity at 200°C (a temperature at which the data in Fig. 3 overlap).

Several observations show some surface segregation of Pt in perovskite. The finer size fractions of flux grown single crystals of $La_{0.7}Pb_{0.3}MnO_3$ tend to have higher Pt content (*2*). This suggests some preferential distribution of Pt during the crystal growing process. Also, we have observed by energy dispersive X-ray analysis in scanning electron microscopy, areas with markedly higher Pt concentration. Croat *et al.* (*10*, *11*) report surface concentrations of Pt 100 times greater than the bulk concentration using ESCA on single crystalline $La_{0.7}Pb_{0.3}MnO_3$. These experiments involved comparing the signal strength of pure metallic Pt with that of the perovskite. This surface concentration is sufficient in their case to account for the observed activity. Finally from the data in Fig. 1 an estimate of Pt at the surface of the crushed crystals can be made. The ratio of the area under the Mn 3*s* lines to that under the Pt 4*f* lines is about 2.8. The photoelectric cross section of the Pt 4*f* lines is about 23 times greater than that of the Mn 3*s* lines. Thus Pt^{4+} occupies about 1.5% of the B sites while in the bulk they occupy about 0.70%. The observed data represent approximately the first five atom layers and if the Pt were further concentrated such that all of the Pt in excess

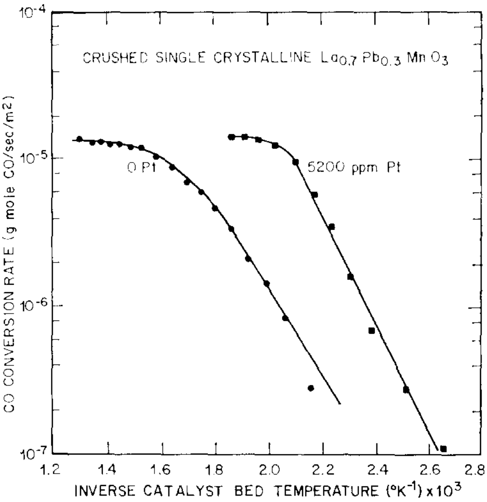

FIG. 3. Activity of $La_{0.7}Pb_{0.3}MnO_3$ with and without Pt.

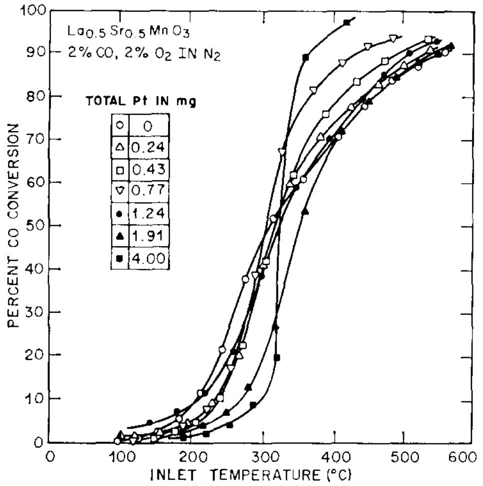

FIG. 4. Activity of supported $La_{0.5}Sr_{0.5}MnO_3$ with various Pt contents (1.1–1.7 g perovskite each).

of 0.70% resided in the first layer, the concentration would be about 7 times that of the bulk (4.7% in the first layer and 0.70% in each of the 4 lower layers averages to 1.5%). The assumption of the concentration from the 5 layers to the top layer is probably optimistic but on the other hand, the broad Pb $5P\ \frac{3}{2}$ line under the Mn 35 peak would distort the background upward and the actual ratio of Mn/Pt may be slightly smaller than measured. However, the approximate 7-fold concentration of Pt is considerably smaller than that observed by Croat *et al.* (*10, 11*) and even when coupled with a further factor of two for the activity of ionic Pt, it is insufficient to account for the 70-fold increase in the activity enhancement over that expected for evenly dispersed metallic Pt. This suggests a synergism between Pt^{4+} in perovskites and the perovskite structure for the oxidation of CO.

Pt on Supported $La_{0.5}Sr_{0.5}MnO_3$ *and* $LaMn_{0.5}Cu_{0.5}O_3$

Since Pt can have a marked effect on the activity of (La,Pb)MnO_3, particularly with SO_2 in the gas stream, other perovskite systems were investigated to find if similar behavior could be observed. The systems $La_{0.5}Sr_{0.5}MnO_3$ and $LaMn_{0.5}Cu_{0.5}O_3$ were chosen because they had previously been shown to offer high activity and stability (*2, 13, 20*). These were prepared by freeze drying, supporting and impregnating with Pt as described earlier.

The activity upon heating after a cycle to 800°C and back of a series of $La_{0.5}Sr_{0.5}MnO_3$ devices with varying Pt contents is shown in Fig. 4 for a gas stream with no SO_2. The activities of these samples are quite close despite the range of Pt, indicating that the major contribution to the activity is the perovskite. The relative order of activity in this closely grouped set of samples does not systematically follow the Pt content. However, the sample with the highest Pt content does show the highest apparent activation energy as indicated by the steep slope.

The effect of adding 50 ppm SO_2 to the gas stream for one of the samples containing Pt is shown in Fig. 5. The initial heating cycle shows a marked deactivation. The cooling curves and subsequent cycles have an activity stabilized at a higher level. For this reason the data to be reported

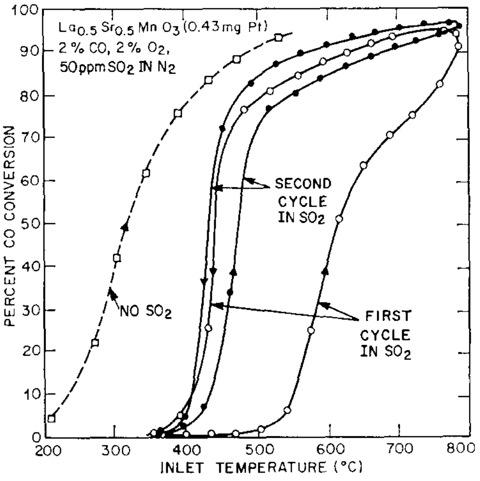

FIG. 5. Activity of $La_{0.5}Sr_{0.5}MnO_3$ (0.43 mg Pt) for the first two heating cycles to 800°C with 50 ppm SO_2 in the reaction gas. (– – –) The activity in the absence of SO_2.

with SO_2 consists of that for the cooling part of the initial cycle with SO_2 in the gas stream.

Such data for the $La_{0.5}Sr_{0.5}MnO_3$ samples is shown in Fig. 6. In contrast to the data in Fig. 4, the samples are well ordered according to the Pt content. Also, as observed in (La, Pb)MnO_3 (*1*, *3*, *6*) the curves tend to be steeper with SO_2 than without.

The activity curves for $LaMn_{0.5}Cu_{0.5}O_3$ with Pt are shown in Fig. 7. As reported elsewhere (*20*) this compound without Pt is an extremely active catalyst for CO oxidation. Note that the onset of the CO oxidation takes place at a little over 100°C. The addition of Pt to this material appears to have a poisoning effect as evidenced in Fig. 7 by a generally lower activity with increasing Pt content. This effect has been observed on samples calcined even to 1000°C. The chlorides of La and perhaps Mn are stable at this temperature while those of Cu and Pt are not. However, since the effect was not observed in $La_{0.5}Sr_{0.5}MnO_3$ it is unlikely that residual chlorides cause the decreased activity. It is speculated that during the reduction of the H_2PtCl_6 metallic Cu is formed which combines with the Pt to form a relatively low activity layer on the perovskite.

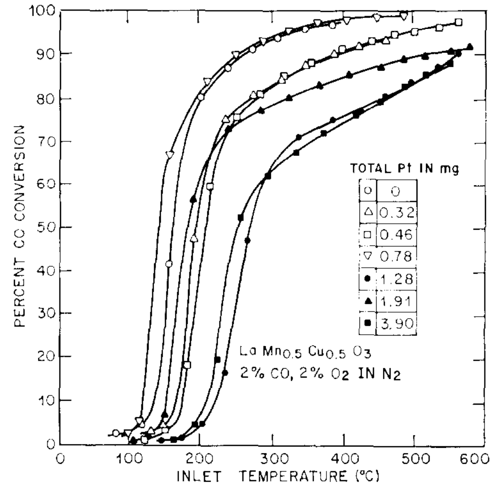

FIG. 7. Stabilized activity of $LaMn_{0.5}Cu_{0.5}O_3$ with various Pt contents (1.1–1.7 g perovskite each).

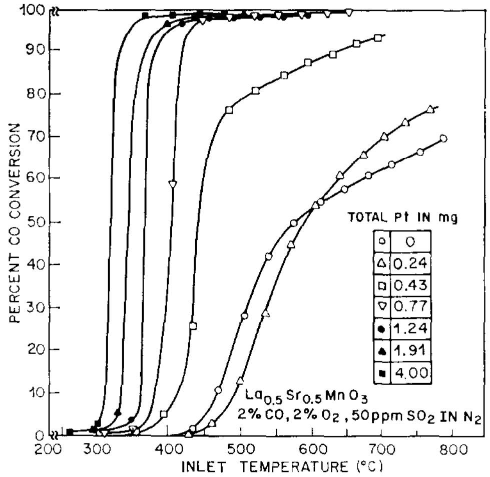

FIG. 6. Stabilized activity of $La_{0.5}Sr_{0.5}MnO_3$ with various Pt contents for SO_2 in the reaction gas (1.1–1.7 g perovskite each).

With SO_2 present the relative activities of the Pt doped $LaMn_{0.5}Cu_{0.5}O_3$ do order themselves according to the Pt present with high Pt giving high activity. However, for equivalent Pt contents these samples are not as active as are the $La_{0.5}Sr_{0.5}MnO_3$ samples.

The activity of these samples and of Pt on "wash coated" supports is shown in Fig. 8 as a function of the total Pt present as measured by chemical analyses. The activity is represented as the temperature at which a 50% conversion of CO is observed. It can be seen that the Pt doped $LaMn_{0.5}Cu_{0.5}O_3$ is relatively inactive while the Pt doped $La_{0.5}Sr_{0.5}MnO_3$ and metallic Pt samples show nearly equivalent activities for a given Pt content. Chemisorption studies show that the Pt on $La_{0.5}Sr_{0.5}MnO_3$ samples have about $\frac{1}{3}$ as much metallic Pt exposed as do the metallic Pt samples while the $LaCu_{0.5}Mn_{0.5}O_3$ samples show little or no chemisorption consistent with a Cu-rich layer on the Pt.

CONCLUSIONS

1. A literature survey has indicated that Pt in (La, Pb)MnO_3 shows a specific activ-

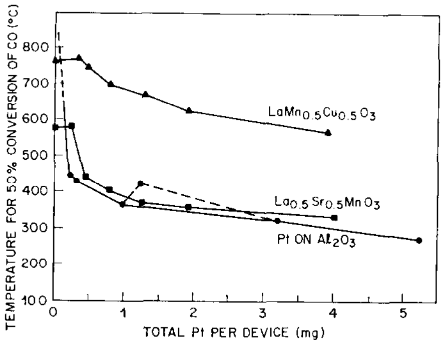

FIG. 8. Activity of supported catalysts for CO oxidation with SO_2 (1.1–1.7 g perovskite).

ity which is higher than that of metallic Pt by as much as a factor of 10^2 if the Pt is assumed homogeneously distributed. Alternately, the specific activity of the Pt may be lower if the Pt is assumed concentrated at the surfaces of the catalyst.

2. ESCA results have shown that Pt in crushed crystalline $La_{0.7}Pb_{0.3}MnO_3$ with 5200 ppm Pt is in the form of dissolved tetravalent Pt. Similar results were observed for a sample of $La_{0.7}Pb_{0.3}MnO_3$ prepared by ceramic techniques to which 5500 ppm Pt were added and reacted at 700°C. Hydrogen chemisorption measurements confirm the absence of metallic Pt for the crushed crystalline samples.

3. The specific activity of Pt^{4+} was measured in $BaPtO_3$ and was found to have about twice the activity of metallic Pt for the oxidation of CO.

4. Measurements have confirmed that the observed activity of Pt doped $La_{0.7}Pb_{0.3}MnO_3$ exceeds that of Pt^{4+} in $BaPtO_3$ by a factor of 70 at 200°C. Various independent observations of Pt segregation at surfaces of the perovskite can explain, in part, the increased activity. Still a model invoking a synergism between dispersed Pt^{4+} and the perovskite to give high specific activities for the available Pt^{4+} is needed to fully explain the observed activity enhancement by Pt.

5. High activity $La_{0.5}Sr_{0.5}MnO_3$ and $LaCu_{0.5}Mn_{0.5}O_3$ on monolithic supports were doped with varying amounts of Pt. In the absence of SO_2 this Pt contributed negligibly to the total activity of the $La_{0.5}Sr_{0.5}MnO_3$ devices. For the $La_{0.5}Cu_{0.5}MnO_3$ devices Pt tended to poison the activity of the perovskite. This was attributed to a Pt–Cu alloy on the surface of the perovskite. Addition of 50 ppm SO_2 to the reaction gas gave the $La_{0.5}Sr_{0.5}MnO_3$ devices an activity proportional to the Pt content. This activity was roughly equivalent to that observed on ceramic supports with equivalent amounts of metallic Pt. With SO_2, $LaCu_{0.5}Mn_{0.5}O_3$ also shows increased activity with increased Pt but a lower level than that observed in $La_{0.5}Sr_{0.5}MnO_3$.

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