Thermochimica Acta, 7 (1973) 303–309

STUDIES OF SOME PEROVSKITE OXIDATION CATALYSTS USING DTA TECHNIQUES*

D. W. JOHNSON Jr. AND P. K. GALLAGHER
Bell Laboratories, Murray Hill, N.J. 07974 (U.S.A.)

(Received 28 May 1973)

ABSTRACT

Differential thermal analysis was used to detect the onset and extent of the catalytic oxidation of 1% hexane and to a lesser extent 3% CO in air. Unsupported catalysts as ground single crystals and in polycrystaline form were selected principally from the system $La_{1-x}M_xMnO_3$ where M = Pb, Ca, Sr, and Ba; although other materials, also having the perovskite structure, were investigated. The catalytic activity of these previously reported materials was confirmed. In general, catalytic activity followed the order Ba ∼ Sr ∼ Ca > Pb. Work over a wide range of x in the Pb system did not indicate a strong variation with x. CO proved easier to oxidize than hexane but generally exhibited similar trends. An acid etch was found to enhance the activity and the effect of subsequent reheating was studied. Catalysts prepared by a variety of techniques were compared.

INTRODUCTION

The catalytic oxidation of carbon monoxide and hydrocarbons is of considerable interest because of the problems associated with automotive emissions. These oxidations occur, for the most part, at the surface of the catalyst and are highly exothermic. Such conditions suggest that differential thermal analysis (DTA) should be a suitable technique for the rapid screening of potential catalysts. Recently Papadatos and Shelstad[1] have used a DTA apparatus to study the catalytic activity of cobalt-metal oxides toward the oxidation of toluene, but operated it in an unconventional isothermal fashion.

In this work we have utilized the technique in its normal dynamic mode to screen potential unsupported catalysts to determine likely candidates for more detailed studies. The catalysts were selected primarily from the system $La_{1-x}M_xMnO_3$ where M = Pb, Ca, Sr, or Ba which have been demonstrated to be generally active catalysts[2,3]. A number of other materials also having the perovskite crystal structure were studied. The materials were tested for their ability to oxidize 1% hexane in air. Occasional comparisons were made using 3% carbon monoxide in air. Neither of these gaseous mixtures is at all similar to actual automobile exhaust but are experimentally convenient to demonstrate the suitability of DTA techniques for screening

---

*This paper was presented before the Division of Petroleum Chemistry of the American Chemical Society and is published with their permission.

potential catalysts. The results therefore should not be extrapolated to indicate performance under actual automotive conditions.

EXPERIMENTAL PROCEDURES

A DuPont model 900 DTA apparatus was used in conjunction with its associated DSC cell. Nitrogen at a rate of 21 $cm^3 min^{-1}$ was saturated with hexane at room temperature and mixed with air to give a combined rate of 500 $cm^3 min^{-1}$ through the DSC cell and over the sample. This corresponds to about 1% hexane. Nominally 15 mg of sample were placed in an aluminum pan and an empty pan was used as a reference. When carbon monoxide was used in place of hexane it was mixed with air to give 3% carbon monoxide.

The heating rate was 10°C min^{-1} to 475°C. Then the sample was cooled at the same rate to about 200°C where the normal cooling rate of the furnace became less than 10°C min^{-1}.

Samples were prepared by a variety of techniques. Ground single crystals were supplied by Mr. J. P. Remeika. Some samples were prepared by mixing weighed quantities of oxides or carbonates and subjecting the mixture to multiple heating and grinding cycles until the x-ray diffraction patterns did not reveal any unreacted materials. A final firing of 1000°C was sufficient. Most samples, however, were prepared by weighing appropriate quantities of the nitrates, dissolving them in distilled water, and then coprecipitating the desired ratio of cations as hydroxides, carbonates, or oxalates. Lanthanum cobaltate(III), lanthanum manganate(III), and praseodymium cobaltate(III) were prepared from the cyanide complex[4]. The precipitates were dried at 120°C in air and calcined at a variety of temperatures to form the desired perovskite phase. X-ray diffraction techniques were used to detect the phases present and the specific surface area of selected powders was measured by the nitrogen absorption (BET) technique.

Selected samples were treated with 5% nitric or hydrochloric acid at 65°C for 5 minutes. The surface area of these etched samples was remeasured.

RESULTS AND DISCUSSION

Because the gas flows over rather than through the sample, there exists a question as to how much of the surface area of the catalyst is available and therefore effective. If it were all effective then the dilution of the active catalyst with inert alumina should lead to a proportional reduction in activity. Figure 1 summarizes the results of such an experiment using $La_{0.5}Pb_{0.5}MnO_3$ prepared by coprecipitation as the hydroxides followed by calcination at 550°C for 16 hours in air. Only heating curves are shown to avoid clutter. The first 50% dilution has very little effect indicating that much of the total catalytic surface area is not utilized.

Several points appeared potentially relevant and useful for comparisons. The onset or lowest temperature of reaction could be determined from the departure of the curve from the baseline, e.g., about 140°C for curve a in Fig. 1. This was deemed too

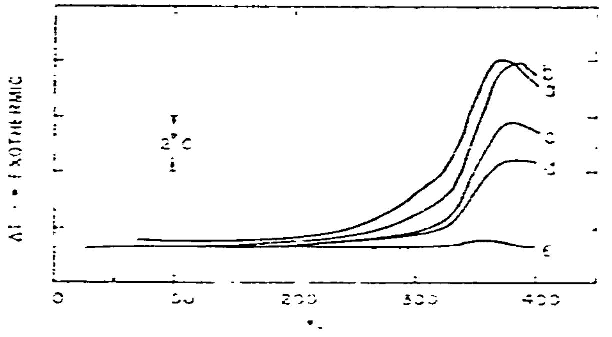

Fig. 1. DTA traces for $La_{0.5}Pb_{0.5}MnO_3$ derived from coprecipitated hydroxides calcined at 540 °C for 16 hours in air and diluted with varying amounts of alumina. Atmosphere is 1% hexane in air. a, 0% Al_2O_3; b, 50% Al_2O_3; c, 75% Al_2O_3; d, 87.5% Al_2O_3; e, 100% Al_2O_3.

subjective, however, for our purposes. The maximum ΔT signal which is eventually reached between 325 and 400 °C is believed to be an indication of the amount of oxidation at the steady state, about 6.6 °C at 365 °C for curve a in Fig. 1, but again this approach has disadvantages. The peak does not always occur at the same temperature for each material. It was finally decided that the temperature at which the ΔT signal indicated a rise of 2 °C in the sample relative to the reference would be a simple and useful parameter with which to compare the activity of our potential catalysts. This point is at 306 °C for curve a in Fig. 1.

The uncertainty in effective surface area shown in Figure 1 does not mean that the effects of relative changes in surface area are not detected. Table 1 illustrates that surface area is still an important factor. X-ray diffraction patterns of these materials revealed only a perovskite phase and thermogravimetric results[5] indicated no appreciable change in oxygen content of the sample over this range of temperature in air.

TABLE 1

EFFECTS OF SURFACE AREA UPON ΔT FOR $La_{0.5}Pb_{0.5}MnO_3$ DERIVED FROM COPRECIPITATED HYDROXIDES CALCINED AT VARIOUS TEMPERATURES

Atmosphere is 1% hexane in air.

Calcination conditions	*Specific surface*	*Temperature where $\Delta T = 2$ °C*
540 °C, 64 hrs., air	19.8 $m^2\ g^{-1}$	332 °C
700 °C, 2 hrs., O_2	9.7	345
900 °C, 2 hrs., O_2	3.6	355

Acid treatment of the material leads to a dramatic enhancement of catalytic activity and an increase in surface area by a factor of 2–8. The nature of this increase in surface area is not obvious from inspection of scanning electron micrographs of etched and unetched samples at a magnification of 10 000. Figure 2 shows repeated DTA traces for etched crushed single crystals of $La_{0.7}Pb_{0.3}MnO_3$. The treatment of

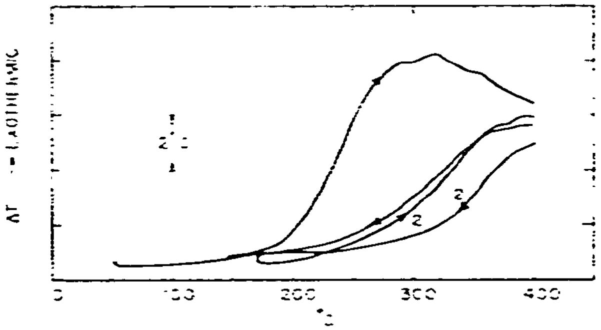

Fig. 2. DTA traces of repeated scans on etched crushed single crystal, $La_{0.7}Pb_{0.3}MnO_3$. 1, first scan; 2, second scan.

this material under these conditions does not appear to be permanent. There is obviously a large hysteresis effect, and the subsequent heating curve following the first cooling curve indicates irreversible damage. The second cooling shows even more loss of activity and this continues to be the case for the third heating not shown here. The surface area is greatly reduced and approaches its original unetched value. This effect was less pronounced with more refractory compositions. Thus, the $La_{0.5}Sr_{0.5}MnO_3$ material prepared from the calcination of coprecipitated carbonates at 1050°C for 2 hours in air exhibits a similar increase in activity upon acid treatment but it is less readily deactivated. Table 2 summarizes some relevant data. Where heating to 475°C for a brief time effectively deactivated the $La_{0.7}Pb_{0.3}MnO_3$ sample, considerably higher temperatures are required to deactivate the $La_{0.5}Sr_{0.5}MnO_3$ material. It should be added that under other conditions more closely resembling actual automobile exhaust the activities of the etched catalysts deteriorate much less. The loss of surface area was in those experiments partly offset by changes in the catalytic activity per unit surface area and by changes in the kinetic parameters of the rate law[6].

TABLE 2

EFFECTS OF ACID TREATMENT AND SUBSEQUENT HEATING UPON $La_{0.5}Sr_{0.5}MnO_3$ PREPARED FROM COPRECIPITATED CARBONATE CALCINED AT 1050°C, FOR 2 HOURS IN AIR

Atmosphere is 1% hexane in air.

Treatment	*T at $\Delta T = 2$ C*	
	Heating	*Cooling*
Unetched	285°C	308°C
Etched	215	236
Heated 500°C/16 hrs./air	230	256
Heated 810°C/2 hrs./air	265	300

Table 3 illustrates variations introduced by the choice of the divalent ion. These materials were prepared by multiple firings of the oxide–carbonate mixtures.

Surface areas were all 2–3 $m^2\ g^{-1}$. The data clearly establish an order of activity Ba∼Sr∼Ca>Pb. The data also indicate that carbon monoxide is more readily oxidized than hexane under these experimental conditions. The relative behavior of the two gases was identical in all of our experiments.

TABLE 3

EFFECT OF VARIATION OF M IN $La_{0.7}M_{0.3}MnO_3$ PREPARED FROM MULTIFIRED MIXTURES OF CARBONATES AND OXIDES

Atmosphere is 1% hexane or 3% CO in air.

M	*T at ΔT = 2°C*			
	Hexane		*CO*	
	Heating	*Cooling*	*Heating*	*Cooling*
Pb	360 °C	385 °C	[a]	[a]
Ca	332	342	328 °C	327 °C
Sr	328	338	291	303
Ba	325	330	285	300

[a] ΔT<2°C.

Little variation was observed with changes in the proportion, *x*, of divalent metal. Table 4 presents some data for the system $La_{1-x}Pb_xMnO_3$ prepared by multiple firings of oxide–carbonate mixtures. Similar behavior was noted with a great variety of coprecipitated strontium or lead substitution with $x = 0.25$ or 0.50 Relative efficiencies varied with precipitating agent and calcination temperature.

TABLE 4

EFFECT OF VARIATION IN *x* IN THE SYSTEM $La_{1-x}Pb_xMnO_3$ PREPARED FROM MULTIFIRED MIXTURES OF CARBONATES AND OXIDES

Atmosphere is 1% hexane in air.

x	*T at which ΔT = 2.0°C*	
	Heating	*Cooling*
0.7	363 °C	367 °C
0.6	365	368
0.5	367	380
0.4	380	385
0.3	360	385

In general there were not particularly significant variations in activity among the various coprecipitates of the same composition. Hydroxides have some advantage in that the perovskite phase can be formed at a lower temperature, around 500 °C, yielding a higher surface area material. When fired at the same temperature, however, hydroxides, carbonates, and oxalates were similar. Coprecipitated material fired to higher temperatures also behaved similarly to that prepared from multiple firings of the oxide-carbonate mixtures so that the preparative technique does not appear to be important once the material has been raised to sufficiently elevated temperatures.

Samples of rare earth transition metal perovskites can be prepared without divalent metal substitution from the cyanides[4]. Table 5 summarizes the DTA results obtained on those prepared in this work. They all show some activity and the low temperature calcine of $LaCoO_3$ is quite good, however, $LaCoO_3$ exhibits greater hysteresis than the others. The $LaCoO_3$ calcined at 500°C is comparable to the divalent substituted manganate calcined at low temperatures for short periods of time.

TABLE 5

ACTIVITY OF SOME RARE EARTH TRANSITION METAL COMPOUNDS PREPARED FROM CYANIDE COMPLEXES

Atmosphere is 1% hexane in air.

Compound	*T of calcination*	*T at $\Delta T = 2.0$°C*	
		Heating	*Cooling*
$LaCoO_3$	500°C	277°C	292°C
	1050	350	363
$PrCoO_3$	500	344	344
	1050	343	349
$LaMnO_3$	900	352	345
	1050	359	348
$LaCrO_3$	1050	375	[a]

[a] $\Delta T < 2$°C.

In general the better unetched samples in the system $La_{1-x}M_xMnO_3$ reached values of $\Delta T = 2$°C around 260–280°C along with $LaCoO_3$. The system $La_{1-x}M_xMnO_3$, however, is more stable than the $LaCoO_3$[3].

CONCLUSIONS

DTA has proved to be a relatively quick and simple means of scanning potential catalysts. When further work on supported systems in conventional reactors was done[5], the relative order of activities was always confirmed.

In the series $La_{1-x}M_xMnO_3$, where M is a divalent ion partially substituted for lanthanum in the perovskite lattice, the catalytic activity for the oxidation of hexane and carbon monoxide follows the order of $Ba \sim Sr \sim Ca > Pb$. The activity is only a minor function of x within the constraints of the perovskite phase.

An acid treatment increases the surface area and greatly enhances the catalytic activity. In the test oxidizing atmospheres described herein these beneficial effects can be destroyed by subsequent thermal treatments at higher temperatures. Strontium substituted materials are more resistive to deactivation materials under these conditions.

Under the DTA conditions where the atmosphere passes over rather than through the sample, the entire surface area of the material is not available or effective. However, the surface area of the sample is still an important factor in its apparent activity.

The sample preparation technique does not appear important other than through its effect upon the attainable surface area of the catalyst.

The activity and stability were not optimized in this study and a more detailed investigation using supported samples and more conventional evaluation techniques is proceeding[5]. DTA has been useful in arriving at the most likely candidates for such studies.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. F. Schrey for measurements of surface area and Mr. D. J. Nitti for assistance in the x-ray work. We also wish to express our appreciation to Messrs. R. J. H. Voorhoeve and J. P. Remeika for helpful discussions.

REFERENCES

1 K. Papadatos and K. A. Shelstad, *J. Catal.*, 28 (1973) 116.
2 R. J. H. Voorhoeve, J. P. Remeika, P. E. Freeland and B. T. Matthias, *Science*, 177 (1972) 353.
3 R. J. H. Voorhoeve, J. P. Remeika and D. W. Johnson, Jr., *Science*, 178 (1973).
4 P. K. Gallagher, *Mater. Res. Bull.*, 3 (1968) 225.
5 P. K. Gallagher and D. W. Johnson, Jr., to be published.
6 R. J. H. Voorhoeve, personal communication, 1972.