# Effect of surface area on CO oxidation by the perovskite catalysts $La_{1-x}Sr_xMO_{3-\delta}$ (M = Co, Cr)

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The catalytic oxidation of carbon monoxide by two compounds in the system $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Co, Cr) was measured at different BET surface areas of the oxide materials. The light-off temperature was found to decrease with increasing surface area up to a certain level beyond which it remained constant for the cobalt-containing compound. This limiting value could not be attained for the chromium-containing compound because of equilibration problems in the preparation. As the active catalytic area as distinct from the total (BET) catalyst area was not clarified, these preliminary results show the need for further inquiry.

**Keywords:** Surface area; CO oxidation; perovskites

## 1. Introduction

Perovskite type oxides based on rare earth oxides of the type $LnMO_3$ have generated considerable interest due to their catalytic activity for the oxidation of CO and $CH_4$ [1–5] and propane [6]. Other oxides like the superconducting systems $La_{2-x}Sr_xCuO_{4-\delta}$ [7] and $YBa_2O_{6+x}$ [8] have also been the subject of catalytic studies. In all these cases it has been generally accepted that increasing the surface area of the oxide materials should increase the catalytic activity of the oxides. There has been an effort to increase the surface areas of the oxides in order to make them comparable to the Pt/alumina supported catalysts (>90 $m^2/g$) currently in widespread use. Several methods have been employed to increase the surface area that are obtainable by conventional solid state processing (yielding areas up to 1 $m^2/g$). These methods include carbonate [9], citrate [9], oxalate [10] precipitation methods, or the Pechini process [11,12] (see below) which yield powders with surface areas of 1–20 $m^2/g$, and freeze drying methods [13] which yield powders with 10–40 $m^2/g$ surface areas.

Among these Arai et al. [3], Barnard et al. [5], and Johnson et al. [13] studied the effects of surface area on the catalytic activity of perovskite oxides; and in all these increasing the surface area was found to decrease the light-off temperature (LOT) required for a given rate of carbon monoxide conversion. Arai et al. [3] found that the 50% $CH_4$ conversion temperature decreased considerably with increasing surface area up to 4 $m^2/g$ for $La_{1-x}A_xMO_3$ (A = Sr, Ba, Ca, Ce; M = Co, Fe, Mn). Further increase in surface areas resulted only in modest decreases of the conversion temperature. A study on CO and propane oxidation by Barnard et al. [5], on the other hand, found an almost linear decrease in the temperature required for 50 and 100% conversion between 6 and 32 $m^2/g$ surface areas with $LaCoO_3$. The results by Johnson et al. [13] indicate that, for some materials like $La_{0.5}Sr_{0.5}MnO_3$, the surface areas do not influence CO conversion as much as the method of preparation.

It has been established that there is an optimum strontium doping level in the perovskite at which maximum catalytic activity is observed [3–5,7]. The optimum doping level in all the strontium-doped perovskites is found to be at 20 mol% Sr approximately. In all cases, however, the activity of even lightly Sr-doped perovskites is higher than that of the undoped perovskites.

Here we report on the catalytic activity of the optimally doped perovskites, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ and $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ at different surface areas. The oxides were prepared by two methods, solid state processing and the Pechini process.

## 2. Preparation

### 2.1. SOLID STATE PROCESSING

The component oxide powders, $La_2O_3$, SrO, CoO (or $Cr_2O_3$), of at least 99.9% purity obtained from Johnson Matthey, were mixed in the desired ratios, ground, pressed into pellets and sintered at the desired temperature for 12 h. The pellets were then reground, pressed, and sintered again. This cycle was repeated three times.

### 2.2. PECHINI PROCESS

Nitrates of lanthanum, strontium, and cobalt (or chromium) were mixed in the proper proportions and dissolved in distilled water. Anhydrous citric acid (2 moles per mole of perovskite) was added to the solution while stirring until a clear solution was obtained. The solution was then heated to 90°C and ethylene glycol (0.67 times amount of citric acid by weight) was added slowly to the solution while stirring constantly. The solution was then heated to 110°C and maintained at that temperature while stirring until all the water evaporated resulting in the formation of a gel. The gel was heated until nitrogen oxide fumes were emitted. When all the fumes were emitted the gel became dry and formed a mixture of lumps and dry powder. The lumps were crushed and ground to form a powder. The powder was then heated to 420°C for 6 h to remove all carbon. The resultant powder was sintered at the desired temperature for the desired time as shown in table 1.

## 3. The reactor

The catalyst powder (0.4 g) was placed in Carberry's gradientless recycle reactor [14] and reacted with a feed gas of 2% CO and 98% $O_2$. The total gas feed rate was 100 ml/min. The temperature was then increased in steps of about 20°C at a rate of 2°C/min. Between the 20° steps the temperature was held constant and the products from the reactor were sampled with a gas chromatograph several times until a constant % CO conversion was attained. It was found that maintaining the temperature constant for 10 min was sufficient to bring the concentrations in the gas phase to constant values. This temperature is used as the light-off temperature (LOT). The results were repeatable to within 2% and the temperature differences at different points on the catalyst bed for this reactor design were found to be less than 1° [14].

## 4. Analysis

The catalyst preparations before and after catalytic reactions were analyzed by X-ray diffraction and single point BET surface area analysis. X-ray diffraction showed each material to be the desired single phase both before and after the reaction while surface areas were not changed by catalytic reaction within an error of ±2%.

Table 1
Preparation parameters for perovskite powders

| Composition | Method | $T_{\mathrm{sint.}}$ (°C) | Time (h) | Surface area ($m^2/g$) |
|---|---|---|---|---|
| $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ | sol. st. | 1200 | 36 | 0.19 |
| $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ | Pechini | 700 | 6 | 4.83 |
| $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ | Pechini | 500 | 6 | 11.5 |
| $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ | sol. st. | 1200 | 36 | 0.91 |
| $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ | Pechini | 1200 | 12 | 1.32 |

## 5. Results and discussion

For the $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ compounds, an increase in the surface area nearly 25 times as much as the solid state processing method (0.19 $m^2/g$) to 4.83 $m^2/g$ was found to decrease the light-off temperature (LOT) required for 50% conversion. This LOT was lowered from 177 to 146°C (fig. 1). Further increase in the surface area did not decrease the LOT but the curve became steeper. These results indicate that a minimum value can be reached in LOT such that increasing the surface area any further will not increase the catalytic activity significantly. We denote this as the saturated LOT. It appears that, in the optimally strontium-doped perovskites, the saturated LOT is reached at lower surface areas than in the undoped perovskites. This conclusion is consistent with the results of Arai et al. [3] for Sr-doped perovskites and Barnard et al. [5] for undoped $LaCoO_3$. For the more catalytically active Sr-doped perovskites, Arai et al. found that the activity increased to a lesser extent with increasing surface area, above 4 $m^2/g$. For the less active undoped sample, $LaCoO_3$, Barnard et al. found an almost linear decrease in LOT with an increase in surface area from 6 to 32 $m^2/g$. To reach saturation in the less active samples, therefore, larger surface areas are required.

Among the $La_{1-x}Sr_xMO_{3-\delta}$ family of perovskites, the $La_{1-x}Sr_xCrO_{3-\delta}$ system was found in this laboratory to be most active catalytically [15]. This system therefore offered the most promise in preparing catalysts with activities comparable to platinum if large surface area powders could be prepared. For the $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ composition, the LOT was decreased from 126 to 121°C by increasing the surface area from 0.91 to 1.32 $m^2/g$ (fig. 2). Further increases in the surface area for this Cr-perovskite system could be achieved by sintering the powder sample from the Pechini process at a lower temperature of 750°C for 6 h. Under these conditions a sample with 3.1 $m^2/g$ surface area was produced. However, although the X-ray diffraction showed a single phase chromite, the color of the sample was green, unlike the material produced by solid state processing where the color of the sample was black. The activity of this sample which was prepared by the Pechini method

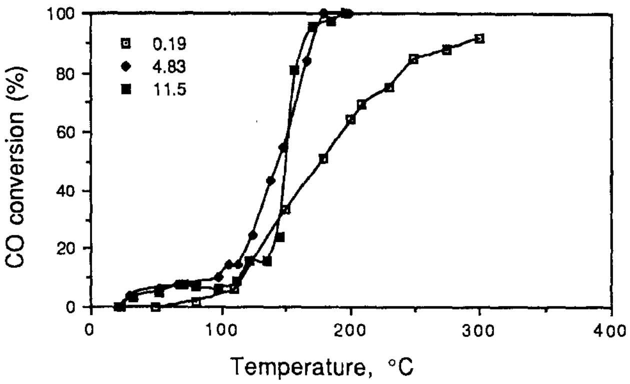

Fig. 1. LOT for Co-perovskite with different surface areas given in $m^2/g$.

(LOT > 250°C) was found to be much lower than other chromites with lower surface areas prepared by the solid state technique that are shown in fig. 2.

Several samples prepared by sintering at lower temperatures had high surface areas, green, and showed reduced catalytic activity. It was found that a sintering above 1050°C was essential to make the samples catalytically active and the resulting product was always black. Changing the atmosphere of sintering from air to pure oxygen did not change this behavior. It is suggested that, when the chromium is in the 4+ state in the perovskite, the samples are black and catalytically active and that when chromium is in the 3+ state the color is green [15]. Further evidence of this was obtained with the unsubstituted Cr-perovskite, $LaCrO_3$ [15].

It can be seen from fig. 2 that the Cr-perovskite showed a gradual change in the conversion of CO in the higher temperature range (170–275°C). One possible explanation for this behavior could be short range concentration gradients present around and within the catalyst particle, since the long range gradients have been eliminated by performing the reaction in a gradientless reactor [14]. Accordingly calculations were performed using the equation suggested by Hidajat et al. [16]. No significant concentration gradients (intra and interphase) resulted from the calculations for the Cr-perovskite used in this study. The other possibility is the effect of temperature on the active catalytic area in contrast to catalyst (BET) area. The catalyst area was found to remain substantially the same after the experiment, however, the same cannot be ascertained for the active catalytic area. It should be pointed out that the active sites have not been established in this class of materials.

It is well known that differences in preparation techniques can lead to different catalytic behavior for the same catalyst phase. In our case we did use two preparation methods, solid state processing and the Pechini process. However, we have tested catalysts of the perovskite and $K_2NiF_4$ families prepared by both methods and have found no difference in catalytic behavior when the sintering temperature during catalyst preparation is high, i.e. > 1050°C [15].

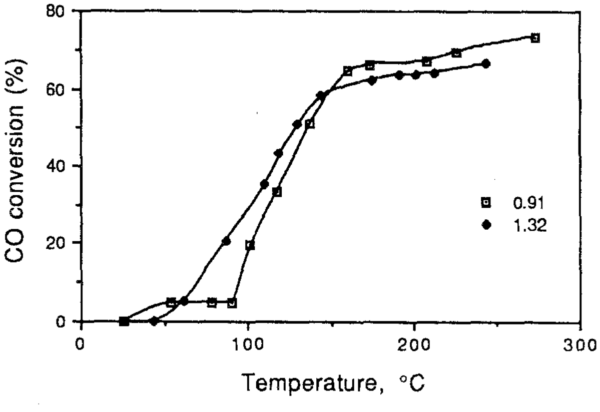

Fig. 2. Effect of surface area on LOT of Cr-perovskite. Surface area given in $m^2/g$.

The results from catalysis experiments are highly dependent on the reaction parameters like flow rate, recycle ratio, composition of the feed gas, removal of selected products during recycling, and the geometry of the reactor itself. Therefore, comparisons between results derived on different reactors are difficult. The comparison then hinges on measuring catalytic activity of a well known material like platinum for each reactor condition. However the mechanisms involved with noble metal catalysts and those involved with oxide catalysts are probably different [17]. For the metal catalysts, oxygen is adsorbed from the gas phase whereas for oxide catalysts [8,18] structural oxygen at or near the surface takes part in the reaction. The lattic oxygen is then replaced by oxygen from the gas phase which regenerates the oxide catalyst. The mechanisms for oxide and metal catalysts are evidently not comparable in such cases.

It has been suggested that the catalytic activity of oxides is influenced by position of the Fermi level when the catalyst participates in a charge transfer reaction [2]. Arai et al. [3] suggested that the bonding strength or electronic states of the material are important for methane oxidation. Since it is difficult to know the exact nature of the "active" sites, it is not possible to compare two materials with an equivalent number of sites nor can a valid comparison be made with the energy levels in a material. If limiting value of saturation temperature can be reached in terms of catalytic activity as was observed in the case of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ by increasing the surface area, then a comparison between the catalytic activity and the semiconductor properties like the position of the Fermi level and the concentration of charge carriers, as suggested by some researchers, is possible. In order to do that, however, the active sites in this class of materials have to be identified as well as the exact reaction scheme. This paper falls far short of that. Further research is required on the exact mechanism of the reactions on these perovskites and similar class of oxides and identification of the active sites because of the importance of these materials in catalysis and electrodes for sensors, fuel cells, magnetohydrodynamic generators, etc.

## 6. Conclusions

A maximum in catalytic activity can be reached in the perovskite oxide systems $La_{1-x}Sr_xMO_{3-\delta}$ (M = Fe, Mn, Co) by increasing the surface area up to a certain limit. For the equivalent Cr-perovskite, $La_{1-x}Sr_xCrO_{3-\delta}$, there is a limit to increasing the surface area due to the relationship between the minimum temperature of sintering required, 1050°C, and a degree of chromium oxidation. This is believed to be due to the formation of $Cr^{4+}$ ions in the sample which appears to influence the catalytic properties significantly. The high temperature catalytic behavior of the Cr-perovskite could not be attributed to concentration gradients in and around the catalyst particle.

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