JOURNAL OF CATALYSIS **140**, 557–563 (1993)

Carbon Monoxide and Methane Oxidation Properties of Oxide Solid Solution Catalysts

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Received July 14, 1992; revised October 29, 1992

The CO and CH_4 deep oxidation properties of the rare-earth-based perovskites, $La_{1-x}Sr_xM_{1-y}B_yO_{3-\delta}$ (M = Co, Cr, Fe, Mn, Y; B = Nb, Ti) and the superconducting systems with the K_2NiF_4 structure, $La_{2-x}Sr_xCuO_{4-\delta}$ and $Nd_{2-x}Ce_xCuO_{4-\delta}$ were investigated. For CO oxidation p-type conducting materials were found to exhibit the highest catalytic activity. For CH_4 oxidation, the activity appears to depend on small electronic conductivity both for p-type and n-type conductors combined with a good oxide ion conduction. © 1993 Academic Press, Inc.

INTRODUCTION

Considerable interest has focused on the catalytic properties of rare-earth-based perovskite oxides of the type $LaMO_3$ since they were found to be catalytically active for the oxidation of CO and CH_4 and reduction of NO_x (*1–3*). This has led to a large effort to study the catalytic properties and to fine tune their properties in order to produce a suitable replacement catalyst for platinum. Previous research indicated that for CO oxidation, increased strontium substitution in $La_{1-x}Sr_xCoO_3$ caused a decrease in catalytic activity due to the generation of more Co^{4+} ions (or p-type carriers). Conversely, increased substitution of lanthanum by cerium in $La_{1-x}Ce_xCoO_3$ resulted in an increase in catalytic activity due to more Co^{2+} ions (n-type carriers) (*1*). Since then, further research has shown that increasing the strontium content actually *increases* the catalytic activity for CO oxidation not only in the $La_{1-x}Sr_xMO_{3-\delta}$ (M = Co, Cr, Fe, Mn; x = substitution on cation site; δ = nonstoichiometry on oxygen site) perovskite system (*4*, *5*) but also in the $La_{2-x}Sr_xCuO_{4-\delta}$ superconducting system (*6*).

For the oxidation of CH_4, the effect of strontium addition is not as clear. Arai *et al.*, (*7*) results indicate that for a $La_{1-x}Sr_xCoO_3$ sample sintered at 850°C strontium addition up to 20 mole% increases the catalytic activity whereas for a similar material sintered at 1200°C, any strontium addition results in a decrease in the catalytic activity. Since strontium additions increase the p-type charge carriers, the role of p-type charge carriers in perovskites on the kinetics of CH_4 oxidation is not clear. The role of n-type conductivity in perovskites on CH_4 oxidation has also not been studied.

In this study we measured the CO and CH_4 oxidation properties for p-type, n-type conducting lanthanum-based perovskites, K_2NiF_4 structures, as well as solid electrolyte compositions in the perovskite family. The results were compared in relation to the type of conduction, the oxidation states of cations, and the magnitudes of ionic and electronic conductivities in the perovskites and other oxides.

EXPERIMENTAL

All the oxides were prepared by the conventional solid-state processing technique. The component oxides were mixed, ground, pressed, and sintered in an alumina crucible between 1000 and 1200°C for 12 hr. The pellets were then crushed, ground, re-

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pressed, and sintered two more times. The grinding and crushing operations were performed in an alumina mortar and pestle. The formation of single-phase compounds was established by X-ray diffraction. The surface areas of the sample were measured before and after the catalytic experiments with a Quantachrome single point BET surface area analyzer. In all cases no noticeable change in surface area was observed for any of the compounds.

Catalytic Reactor

The conditions for catalytic measurements for each composition were the same. Each catalyst powder composition was sieved with a 320-mesh screen and the screened powder was used as catalyst. The amount of catalyst used was 0.4 g. The feed gas composition was 2% CO and 98% O_2 for CO oxidation and 2% CH_4 and 98% air for methane oxidation. The total gas feed rate was 100 ml/min. The catalytic reactor was a recycled gradientless reactor. The recycle ratio was always maintained at 50 times the feed rate for CO oxidation and for CH_4 oxidation. Further details of the reactor are available elsewhere (*8*). The temperature was raised above room temperature in steps of about 20°C at a rate of 2°C/min. Between the 20°C steps the temperature was held constant and the products from the reactor were sampled with a gas chromatograph several times until a constant conversion was attained. It was found that maintaining the temperature constant for 10 min was sufficient to equilibrate the concentrations in the gas. If no time was allowed for equilibrium but the temperature was ramped up continuously at 2°C per min, it was found that the 50% conversion (light-off temperature) occurred at about 20°C lower temperature than by the equilibrium method. Since this is not steady state, all the measurements were performed at steady state by keeping the temperature constant for each sampling. After catalytic experiments, the spent oxides were analyzed by X-ray diffraction and were found to be the same single phase as the starting material.

RESULTS AND DISCUSSION

All experiments were preceded by running a blank experiment to ascertain no catalytic activity due to contamination in the reactor.

CO Oxidation

The list of compounds employed in the measurements along with their surface areas, principal conduction mode, and the light-off temperature (LOT for 50% conversion) for CO oxidation are given in Table 1. Since the maximum conversion in some cases is less than 50%, the percentage conversion at the maximum temperature studied is indicated in the table in parenthesis.

In some oxides both p- and n-type conduction is possible depending on the impurity ions present in the compound and the oxygen potential in the gas phase. In such cases the conduction type denoted is either n, p or p, n, where the first letter indicates the known conductivity type for a pure compound in air at the temperature of operation of the catalytic reactor and the second letter denotes the other possibility, which depends on the concentration of the impurities and reducing atmospheric conditions. For the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system, the powders were obtained from Dr. Smyth (*9*). The

TABLE 1

Light-off Temperature (LOT) for CO Oxidation

Composition	Conduction type	LOT (°C)	Surface area (m^2/g)
$La_{0.8}Sr_{0.2}CrO_{3-\delta}$	p	136	0.91
$La_{0.8}Sr_{0.2}FeO_{3-\delta}$	p, n	228	0.28
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	p, n	177	0.20
$La_{0.8}Sr_{0.2}MnO_{3-\delta}$	p, n	234	1.36
$La_{0.8}Sr_{0.2}YO_{3-\delta}$	p, Electrolyte	363 (6.5%)	0.30
Pt/alumina	Metal	108	96
$Nd_2CuO_{4-\delta}$	n, p	181	1.04
$Nd_{1.9}Ce_{0.1}CuO_{4-\delta}$	n	299 (46%)	0.34
$Nd_{1.8}Ce_{0.2}CuO_{4-\delta}$	n	310 (33%)	0.28
$La_2CuO_{4-\delta}$	p, n	239	Data from Ref. (*6*)
$La_{1.8}Sr_{0.2}CuO_{4-\delta}$	p	205	Data from Ref. (*6*)
$La_{1.6}Sr_{0.4}CuO_{4-\delta}$	p	192	Data from Ref. (*6*)

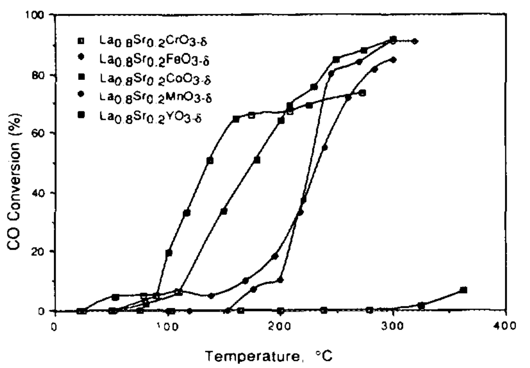

FIG. 1. CO oxidation by A-site-substituted perovskites.

properties and defect chemistry of the system $Nd_{2-x}Ce_xCuO_{4-\delta}$, are published elsewhere (*10*). The catalytic oxidation data on the p-type superconducting system, $La_{2-x}Sr_xCuO_{4-\delta}$, were obtained from the authors in Ref. (*6*).

For the perovskite systems, $La_{1-x}Sr_xMO_{3-\delta}$ (M = Co, Cr, Fe, Mn, Y), the LOT results for CO oxidation are shown in Fig. 1 and can be compared with that of Pt/Al_2O_3 catalyst in Fig. 2. While the Cr-perovskite showed the lowest LOT and close to that of Pt/Al_2O_3, it should be noted that the surface area of the supported Pt catalyst is at least two orders of magnitude higher than those of the oxides. Under the conditions of low temperature (100–300°C) and the feed-gas composition, all the oxides are p-type conductors. However, $La_{0.8}Sr_{0.2}YO_{2.9}$, is a relatively poor conductor at these low temperatures. This material, which is a solid electrolyte, was found to be a very poor catalyst for CO oxidation, with minimal conversion up to 300°C.

Among the superconducting oxide systems, the p-type conductors, $La_{2-x}Sr_xCuO_{4-\delta}$ exhibited much lower LOT than the n-type superconducting oxides, $Nd_{2-x}Ce_xCuO_{4-\delta}$, as shown in Fig. 2. Also, as the strontium content is increased in $La_{2-x}Sr_xCuO_{4-\delta}$, the concentration of p-type charge carriers is increased, and this corresponds to a lower LOT. Similarly, as the cerium substitution is increased in $Nd_{2-x}Ce_xCuO_{4-\delta}$, the concentration of n-type charge carriers is increased, and this is found to correspond to a higher value of LOT.

From Figs. 1 and 2 it is obvious that p-type charge carriers result in lower temperatures for CO conversion. This suggests that the activation of carbon monoxide on the catalysts can be described by the adsorption process,

$$CO_{(g)} + \dot{p} = CO^{+}_{(ad)}, \qquad (1)$$

where $\dot{p}$ denotes a hole. This reaction may be the controlling factor in CO oxidation by perovskite oxides. The p-type conductivity

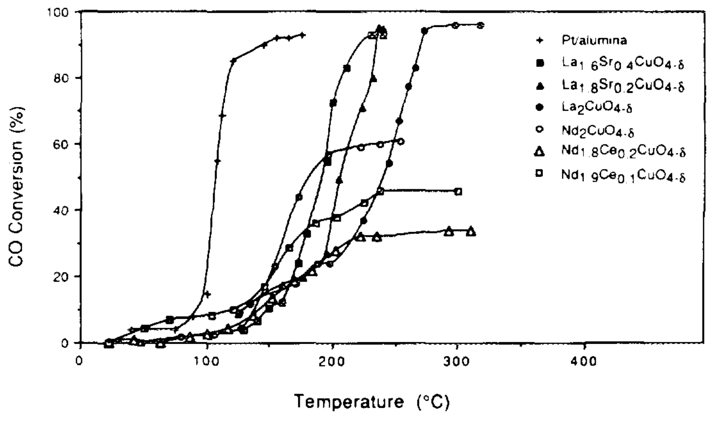

FIG. 2. CO oxidation by superconducting oxides.

of the solid electrolyte, $La_{0.8}Sr_{0.2}YO_{2.9}$, is very low at these temperatures and, therefore, does not contribute any charge carriers to aid the catalytic oxidation reaction (1).

CH_4 Oxidation

The catalytic oxidation of CH_4 was measured for all the perovskite oxides, $La_{0.8}Sr_{0.2}MO_{3-\delta}$, and the superconducting oxide $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ as catalysts and compared with the activity of 0.5% palladium and 0.5% platinum supported on alumina. The surface areas of the oxides are as given earlier in Table 1. Unlike the case of CO oxidation, here, the activity of the chromite, $La_{0.8}Sr_{0.2}CrO_{3-\delta}$, is lower than that of all the other perovskites. Among the electronically conducting perovskites, it is only in $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ that the lowest B-site cation oxidation state is 3+ (Cr^{3+}) down to an oxygen partial pressure of 10^{-22} atm (*11*), which was the lowest oxygen pressure employed in the reference. Therefore, $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ remains a p-type conductor in both reducing and oxidizing atmospheres (*12*). In the case of the other oxides, the B-site cations can be reduced to a lower oxidation state, 2+ (Cu, Fe, Mn, Co) or 1+ (Cu). Therefore, under reducing conditions, these materials can also generate n-type charge carriers.

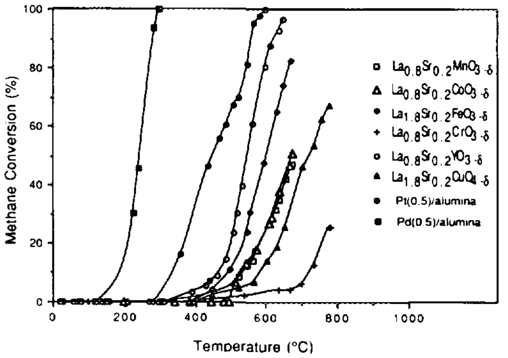

FIG. 3. Methane oxidation by A-site-substituted perovskites.

In order to study the effect of n-type materials with a similar perovskite structure on the oxidation of CH_4, B-site-substituted perovskites were fabricated by substituting Nb and Ti in place of Cr and Fe to give the following compositions: $LaFe_{0.8}Nb_{0.2}O_{3-\delta}$, $LaFe_{0.8}Ti_{0.2}O_{3-\delta}$, and $LaCr_{0.8}Nb_{0.2}O_{3-\delta}$. The first two perovskites, $LaFe_{0.8}Nb_{0.2}O_{3-\delta}$ and $LaFe_{0.8}Ti_{0.2}O_{3-\delta}$, are mainly n-type conductors except under highly oxidizing conditions where they exhibit p-type conduction behavior (*12*). $LaCr_{0.8}Nb_{0.2}O_{3-\delta}$, while p-type, has lower conductivity than the highly conductive, p-type, $La_{0.8}Sr_{0.2}O_{3-\delta}$ (*12*). Methane oxidation by A-site-substituted perovskites is shown in Fig. 3. The catalytic activity of these B-site perovskites for methane oxidation is shown in Fig. 4, in comparison with some of the p-type A-site-substituted perovskites. The results indicate high activity for the Fe-based perovskites. Both the A-site-substituted and B-site-substituted Fe-based perovskites showed higher activity than other perovskites. However the other B-site-substituted Fe-based perovskite, $LaFe_{0.8}Ti_{0.2}O_{3-\delta}$ exhibited reduced activity for CH_4 oxidation.

Finally the catalytic properties of three solid electrolytes were measured, Fig. 5. The electrolyte, $La_{0.8}Sr_{0.2}YO_{2.9}$, exhibited the highest catalytic activity for CH_4 oxidation compared to all the other oxides, whereas $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ did not show significant activity, and $(Bi_2O_3)_{0.8}(SrO)_{0.2}$ was totally inactive. Among these electrolytes, only $La_{0.8}Sr_{0.2}YO_{2.9}$ is a p-type conductor for oxygen partial pressures above 10^{-6} atm (*13*). Below this oxygen pressure it is an electrolyte. The other two electrolytes are purely ionic conductors at high oxygen partial pressures. At oxygen pressures below 10^{-20} atm, it is well known that stabilized zirconia becomes an n-type conductor, and $(Bi_2O_3)_{0.8}(SrO)_{0.2}$ is reduced below an oxygen pressure of 10^{-15} atm.

The results of Figs. 3, 4, and 5 were then compared and evaluated in terms of the following known properties of the oxides:

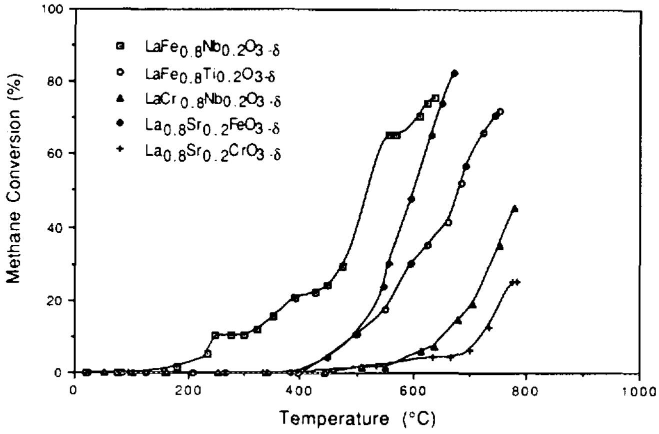

FIG. 4. Methane oxidation by B-site- and A-site-substituted perovskites.

(1) type of charge carriers, e.g., p-type or n-type;

(2) existence of ($La_{0.8}Sr_{0.2}$) ion at A-site;

(3) existence of more than two oxidation states for B-site cations;

(4) oxygen vacancy concentration;

(5) oxygen diffusion coefficient;

(6) conductivity.

The type of charge carriers predominant in ambient conditions is shown in Table 1. In some perovskite oxide compounds, more than one type of conduction is possible, depending on the temperature and oxygen partial pressure. In such cases the charge carriers predominant in air at the temperature of operation are denoted first, followed by the charge carriers which are probably predominant in reducing environments. For example, $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ is a p-type conductor in the oxygen partial pressure range 1 to 10^{-12} atm and n-type below 10^{-12} atm (*14*). Therefore, in this case the conduction type is denoted as "p, n." Similarly $La_{0.8}Sr_{0.2}YO_{2.9}$ is denoted as "p, electrolyte," since it is p-type above 10^{-6} atm (*13*) and an electrolyte under reducing environments. From Figs. 3, 4, and 5 it is found that the type of charge carriers is not important, considering that the p-type $La_{0.8}Sr_{0.2}YO_{2.9}$ is very active for CH_4 oxidation and so too is n-type $LaFe_{0.8}Nb_{0.2}O_{3-\delta}$, whereas p-type $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ exhibits very little activity.

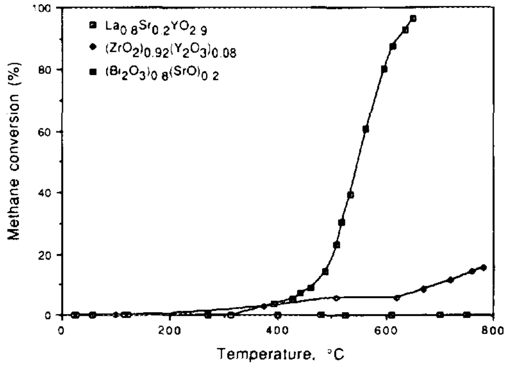

FIG. 5. Methane conversion over electrolytes.

If the catalytic activity were dependent mainly on the well known active A-site ions La (as in La_2O_3) and Sr, then all the compounds with the composition as La or $La_{0.8}Sr_{0.2}$ on the A-site should be more active than others. This is also not the case, since the most active, $La_{0.8}Sr_{0.2}YO_{2.9}$, and one of the least active materials, $La_{0.8}Sr_{0.2}CrO_{3-\delta}$, both have A-site composition, $La_{0.8}Sr_{0.2}$.

Some of the B-site cations can exist in multiple oxidation states. For example, the known oxidation states for Mn are 2,3,4. In the case of $La_{1-x}Sr_xCrO_{3-\delta}$, Cr was calculated to exist in two oxidation states, 3 and 4 (*11*). Similarly the other B-site cations with more than two oxidation states are Fe (2,3,4), Co (2,3,4), and Cu (1,2,3). Compounds with one of these ions exhibit a wide range of catalytic activity for CH_4 oxidation, ranging from poor for $La_{0.8}Sr_{0.2}BO_{3-\delta}$ (B = Co, Mn) to very good for $La_{0.8}Sr_{0.2}FeO_{3-\delta}$. Second, $La_{0.8}Sr_{0.2}YO_{2.9}$ without three oxidation states is more active than compounds with Fe, Co, Cr, Mn, or Cu as B-sites. Therefore, multiple oxidation states are not an important factor in catalytic activity. It should be noted that multiple oxidation states give rise to the existence of both p- and n-type conductivity in the material.

The oxygen vacancy concentration may be important for catalytic activity if an incorporation of oxide ions from the reactions at the surface into the lattice can increase the activity of the material. The oxygen vacancy concentration is known to be very small in the electronic conductors in ambient conditions. Only the electrolytes, $La_{0.8}Sr_{0.2}YO_{2.9}$, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ and $(Bi_2O_3)_{0.8}(SrO)_{0.2}$ have significant oxygen vacancy concentrations. For example, in $La_{0.8}Sr_{0.2}YO_{2.9}$, 3.45% of the oxygen sites are vacant, whereas for $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ it is 2.04% and for $(Bi_2O_3)_{0.8}(SrO)_{0.2}$, 7.14% of oxygen sites are vacant. Only $La_{0.8}Sr_{0.2}YO_{2.9}$ among the electrolytes with significant oxygen vacancy concentration is active, therefore oxygen vacancy concentration is not a predominant factor for CH_4 catalytic activity.

Compared to CO oxidation which occurs at temperatures below about 300°C, CH_4 oxidation takes place at a higher temperature ($T > 450°C$) in the perovskite oxides. The oxide ion diffusion coefficients then become important if the lattice oxygen takes part in the reaction. The oxide ion diffusion coefficients have been summarized in a previous study (*15*). The values are comparable for the electronically conducting perovskites and the electrolytes. Therefore, this is also not a predominant factor by itself.

The conductivities of the p-type electronic conductors in air can be divided into three groups, which in approximate decreasing order of conductivity are:

(i) $La_{0.8}Sr_{0.2}CoO_{3-\delta}$, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, $La_{0.8}Sr_{0.2}CrO_{3-\delta}$;
(ii) $La_{0.8}Sr_{0.2}FeO_{3-\delta}$, $LaFe_{0.8}Nb_{0.2}O_{3-\delta}$, $LaFe_{0.8}Ti_{0.2}O_{3-\delta}$;
(iii) $La_{0.8}Sr_{0.2}YO_{2.9}$.

Further information on the conductivity of these materials is available elsewhere (*12*, *15*) and references therein. From the above list, groups (ii) and (iii) are more active than group (i). Therefore, the most active catalysts are those which exhibit p-type conductivity, but with a lower magnitude of conductivity. Electronic conduction is, however, essential, since the pure electrolytes, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ and $(Bi_2O_3)_{0.8}(SrO)_{0.2}$, showed poor activity compared to the electronic conductors. The contributions from electronic and conductivities in oxides for which data are available or could be extrapolated are given in Table 2. The compositions are listed in increasing order of electronic conductivity. The compounds with the lowest and highest electronic conductivities are poor catalysts, whereas $La_{0.8}Sr_{0.2}YO_{2.9}$ and $La_{0.8}Sr_{0.2}FeO_{3-\delta}$, with small electronic conductivities in the middle of the semiconduction range combined with good ionic conduction, are active catalysts.

TABLE 2

Electronic and Ionic Conductivities of Selected Oxides

Composition	Temperature (°C)	σ_{ion} (S/cm)	σ_{el} (S/cm)
$(Bi_2O_3)_{0.8}(SrO)_{0.2}$ (*15*)	800	0.2	~0
$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (*16*)	800	5×10^{-3}	~0
$La_{0.8}Sr_{0.2}YO_{2.9}$ (*13*)	800	2×10^{-4}	1.45×10^{-3}
$La_{0.8}Sr_{0.2}FeO_{3-\delta}$	800	10^{-2}[a] (*17*)	15–30[a] (*18*)
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	800	10^{-2}	10^3 (*19*)

[a] Extrapolated from published data.

Among the active oxide catalysts in this study, $La_{0.8}Sr_{0.2}YO_{2.9}$ is also a proton conductor, as is the active metal, Pd. In order to investigate the possibility that protonic conduction may enhance methane oxidation, another proton conductor, β-$Ca(PO_3)_2$ was prepared and analyzed. The details of the preparation method and properties of β-$Ca(PO_3)_2$ are available elsewhere (*20*). This sample was found to be completely inactive up to 800°C. Therefore, proton conduction is not a predominant factor for catalytic activity in the oxidation of methane.

CONCLUSIONS

Among the perovskites and related oxides studied for catalytic oxidation of CO, highly conductive p-type materials were found to have the highest activity. This is attributed to be due to the importance of a reaction involving holes from the catalyst composition.

For CH_4 oxidation, it was found that the catalytic activity is enhanced by small p-type or small n-type conductors which exhibit poor electronic conductivity combined with good oxide ion conduction. These include $La_{0.8}Sr_{0.2}YO_{2.9}$ and $LaFe_{0.8}Nb_{0.2}O_{3-\delta}$. It was thus established that the presence of high conductivity is detrimental to catalytic activity for CH_4 oxidation exhibited by some of the perovskite oxides and K_2NiF_4 superconducting oxides.

ACKNOWLEDGMENTS

The authors acknowledge financial support from Amoco Research Corporation for this and continuing research efforts.

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