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SOLID OXIDE SOLUTIONS AS CATALYSTS –A COMPARISON WITH SUPPORTED Pt

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Solid oxide solutions (SOS) of La, Sr and Cr of the formula $La_{1-x}Sr_xCrO_{3-\delta}$ (where δ is the deviation from stoichiometry and $0 < x < 0.5$) exhibit catalytic activity for oxidation (CO-oxidation) which rivals that of a highly dispersed 0.5% Pt/alumina fume abatement catalysts. Hydrogenation (of propylene) activity is also manifest with the SOS formulation. Exposure of the SOS catalyst to H_2S does not reduce catalytic activity.

1. Introduction

Platinum and other noble metals play dominate roles in oxidation and reduction catalysis. Thus we find highly dispersed Pt on alumina a major component in the automotive exhaust fume abatement reaction (catalytic converter) and in reforming of petroleum stocks.

Given it's limited supply, and precious nature (and therefore high cost) the search for alternatives to Pt is a continuing enterprise. In fact less expensive base metal oxides were early candidates for the automobile catalytic converter until their susceptability to sulphur poisoning became manifest. Hence the use of Pt inspite of it's sintering characteristics which limit converter life. Sintering, the thermally induced-growth of crystallite size with consequent activity decline, plagues all high temperature supported metal (e.g. Pt) catalyzed processes. A noble metal catalyst substitute should exhibit activity comparable to the noble metal while being impervious to sulphur poisoning and sintering.

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Shortly after Meadowcroft reported the use of strontium doped $LaCoO_3$ as a low cost oxygen electrode material comparable to Pt [1], testing of catalytic activity of rare earth manganites and cobaltites on certain gas systems was carried out [2]. Although potential substitutes for Pt catalysts had been reported thereafter [3–5], the noble metal catalyst have not yet been replaced successfully.

However, solid solutions of strontium-doped $LaCrO_3$ and La_2CuO_4 were tested in our laboratory for the oxidation of carbon monoxide, the main toxic constituent of automotive exhaust. They show catalytic activity similar to the Pt/alumina catalyst, thus these solid solutions seem very promising substitutes for Pt in catalytic devices for the treatment of automobile exhaust and allied pollution abatement processes.

Further, our solid oxide solution (SOS) catalyst exhibits good activity in hydrogenation of propylene.

2. Catalyst preparation

Solid solutions of $La_{2-x}Sr_xCuO_{4-\delta}$ and $La_{1-x}Sr_xCrO_{3-\delta}$ were prepared by the conventional ceramic technique. The constituents were quantitatively mixed in the proper ratio and pellets were prepared by pressing the mixture. Each pellet was sintered in an alumina crucible under air for 12 hours at the appropriate temperature. Cycles of grinding, pelletizing and heating were repeated three times on each sample to ensure complete reaction. For $La_{2-x}Sr_xCuO_{4-\delta}$ the sintering temperature was 1050 °C to 1100 °C and for the $La_{1-x}Sr_xCrO_{3-\delta}$ it was 900–920 °C. X-ray diffraction, SEM and EDX showed that each sample was a homogeneous single phase. All the component oxides used were 99.99% Puratronic speciality products from AESAR (Johnson Matthey). The 0.5% Pt on gamma alumina was supplied by Engelhard Industries, Inc. Uniform mesh size of powder (sieve fraction between 10 μm and 35 μm) was used for the catalytic studies. Surface area of the solid solutions were measured by the BET N_2 adsorption technique and the Pt site counting on Pt/alumina catalyst was done by CO chemisorption as well as hydrogen-oxygen titration.

3. Experimental

Temperature programmed catalytic studies were carried out in the Notre Dame multifunctional *in situ* catalyst characterization unit [6]. The tests were made with a fixed feed concentration of the gas mixture (1% CO in oxygen through a fixed amount of powdered catalyst (0.25 g) to maintain constant contact time. The conversion of CO was determined as a function of temperature while the catalyst was temperature programmed (2 °C/min). The effluent from the gradientless recycling reactor was sampled using a zero volume sampling valve at different time intervals and analyzed by means of a gas liquid chromatograph interphased with an automatic integrator.

Temperature programmed hydrogenation of propylene was carried out with a fixed feed concentration of the gas mixture (3.8% propylene in hydrogen) through a fixed amount of powdered catalyst (0.29 g) to maintain constant contact time. Propane was the only product formed in the temperature range of our study. The conversion of propylene and the formation of propane were determined as a function of temperature. Propylene and propane were separated and analyzed using a Hayesep Q80/100 chromatographic column. In the comparisons with Pt, the weight of Pt/Al_2O_3 used was 0.12 grams.

4. Results

The activity of the various fresh catalysts are given in table 1 as the temperature at which 50% conversion of CO was reached for a constant amount of catalyst. Solid solutions of $La_{2-x}Sr_xCuO_{4-\delta}$ are *less active than that of* $La_{1-x}Sr_xCrO_{3-\delta}$. The solid solutions show a significant difference in catalytic activity from the individual oxides. *Results show that a suitable combination of the individual oxides form a solid solution (La, Sr, Cr_2O_3) close to the catalytic property of the noble metal catalyst.* Also the activity of the solid solutions of $La_{1-x}Sr_xCrO_{3-\delta}$ is very similar to that of Pt/alumina catalyst. Two combinations of these solid solutions were synthesized and the catalytic kinetics of CO

Table 1
Activity of the oxidation catalysts for CO oxidation
Flow rate 100 ml/min of a 1% CO in oxygen at normal temperature and pressure. Weight of Pt/Al_2O_3 catalyst = 0.12 g, that of other catalysts = 0.25 g.

Catalyst	La/(La + Sr)	Activity (Temperature for 50% CO conversion) (°C)
$CuSrO_2$	0	227
$LaSrCuO_{4-\delta}$	0.5	212
$La_{1.6}Sr_{0.4}CuO_{4-\delta}$	0.8	192
$La_{1.8}Sr_{0.2}CuO_{4-\delta}$	0.9	202
$La_{1.9}Sr_{0.1}CuO_{4-\delta}$	0.95	201
La_2CuO_4	1.0	240
CuO	–	146
La_2O_3	–	192
SrO	–	244
ND1 ($La_{0.8}Sr_{0.2}CuO_{3-\delta}$	–	122
ND2($La_{0.7}Sr_{0.3}CuO_{3-\delta}$)	–	139
ND1(exposed to H_2S)	–	128
0.5%Pt/alumina	–	98

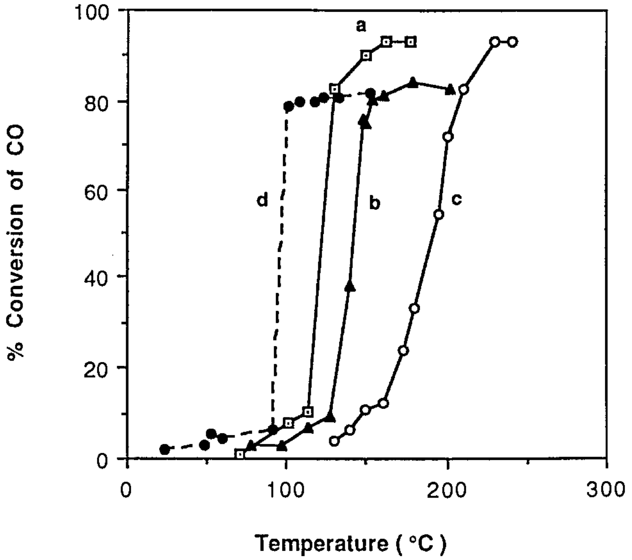

Fig. 1. Light-off temperature curves of CO oxidation for (a) ND1 ($La_{0.8}Sr_{0.2}CrO_{3-\delta}$), (b) ND2($La_{0.7}Sr_{0.3}CrO_{3-\delta}$); (c) $La_{1.6}Sr_{0.4}CuO_{4-\delta}$ and (d) Pt/alumina catalysts. 1% CO concentration in feed.

oxidation on these compositions were extensively studied. The results of the temperature programmed catalytic study of $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ (abbreviated as ND1) and $La_{0.7}Sr_{0.3}CrO_{3-\delta}$ (abbreviated as ND2) are compared with Pt/alumina in fig. 1. The activity pattern of the solid solutions can be seen to be very similar to that of the Pt/alumina catalyst. Also the kinetic analysis of CO oxidation on these solid solutions results in the same Langmuir-Hinshelwood model as that of the Pt/alumina catalyst.

Propylene hydrogenation conversion vs. temperature for ND1 is set forth in fig. 2 as are also shown the data over fresh and partially sintered Pt/Al_2O_3. ND1 is patently less active than even sintered Pt yet exhibits kinetic behavior (simple Langmuir-Hinshelwood) similar to the Pt catalyst.

Be it noted that the SOS catalysts, in contrast with supported Pt, cannot sinter at typical conditions of catalysis (temperatures < 800 ° C) since the SOS catalysts are synthesized at temperatures above 1000 ° C.

A comparison of specific activity for CO oxidation over Pt and ND1 and ND2 is set forth in table 2. Specific activity is reaction velocity (moles/contact time) per exposed catalyst area at 50% CO conversion. For Pt/Al_2O_3 chemisorption or titration grants a value of Pt area i.e., catalyst area exclusive of support. As we do not at this time know what portion of the total (BET) area of the SOS is the actual catalyst area, we are obliged to use the SOS BET area in evaluating its specific activity. Temperature differences are ignored in the rough comparison given in table 2. It, the comparison, suffices to suggest that ND1 at 122 ° C surely rivals Pt/Al_2O_3 at 100 ° C in terms of reaction velocity per unit of catalyst

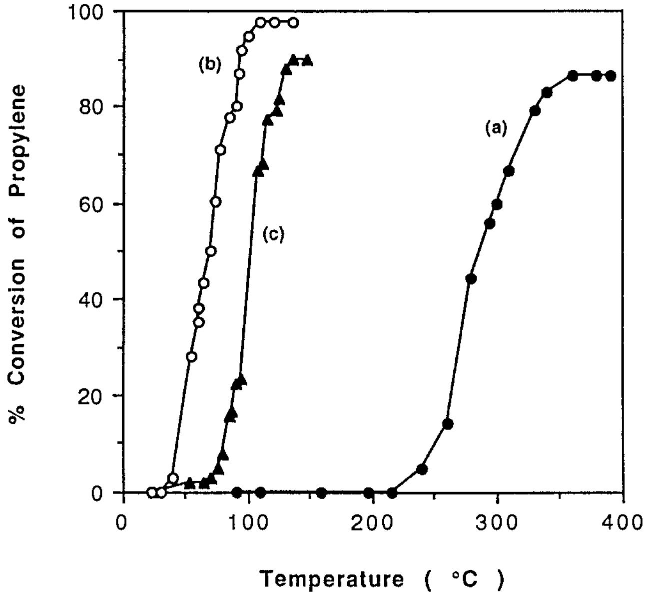

Fig. 2. Light-off temperature curves of propylene hydrogenation for different catalysts. (a) ND1 ($\mathrm{La_{0.8}Sr_{0.2}CrO_{3-\delta}}$) (b) Fresh 0.5% Pt/alumina (c) Pt/alumina sintered at 600 °C. 3.8% propylene concentration in the feed.

exposed area. Given that Pt will sinter with time-on-stream whilst ND1 will not *and* techniques of SOS preparation which promises higher BET areas are presently being studied, the comparison of Pt and SOS catalysts can become only more favorable for the SOS candidates.

We realize that the threat of susceptibility to sulfur poisoning in an oxidation atmosphere is a serious drawback to the use of any metal oxide catalyst. ND1 was tested for CO oxidation activity after it had been exposed to H_2S at room temperature for 12 hours. Following that exposure to H_2S the catalyst (ND1) retained the same CO oxidation activity as that of the fresh catalyst (ND1) which had not been exposed to H_2S (table 1).

Table 2
Specific activity of the oxidation catalysts at 50% conversion

Catalyst	Wt. of the catalyst (g)	BET area (m^2/g)	Exposed area (m^2)	Specific activity (moles of CO/m^2h)
Pt/alumina	0.12	249	$0.27^{@}$	0.04
			0.47^{a}	0.02
ND1($\mathrm{La_{0.8}Sr_{0.2}CuO_{3-\delta}}$)	0.25	0.33	0.08^{b}	0.02
ND2($\mathrm{La_{0.7}Sr_{0.3}CuO_{3-\delta}}$)	0.25	0.35	0.09^{b}	0.02

[@] Specific surface area of Pt measured by CO chemisorption technique.
[a] Specific surface area of Pt measured by hydrogen-oxygen titration technique.
[b] (BET area) (0.25).

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References

[1] D.B. Meadowcroft, Nature 226 (1970) 847.
[2] W.F. Libby, Science 171 (1971) 499.
[3] L.A. Peedersen and W.F. Libby, Science 176 (1972) 1355.
[4] R.J.H. Voorhoeve, J.P. Remeika, P.E. Freeland and B.T. Matthias, Science 177 (1972) 353.
[5] R.J.H. Voorhoeve, D.W. Johnson, Jr., J.P. Remeika and P.K. Gallagher, Science 195 (1977) 827.
[6] C. Serrano and J.J. Carberry, Appl. Catal. 19 (1985) 119.