Catalytic decomposition of nitrous oxide over perovskite type solid oxide solutions and supported noble metal catalysts

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The catalytic decomposition of nitrous oxide to nitrogen and oxygen has been investigated over various solid oxide solutions (SOS), $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Cr, Fe, Mn, Co or Y), $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and supported Pd, Pt catalysts. The reaction was carried out in a gradientless recycle reactor at 1 atm pressure with a feed gas containing about 0.5% N_2O (in helium). Among the various solid solutions, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ showed a maximum N_2O conversion of 90% at 600°C. The order of activity observed for N_2O decomposition was $La_{0.8}Sr_{0.2}CoO_{3-\delta} > La_{0.8}Sr_{0.2}FeO_{3-\delta} > La_{1.8}Sr_{0.2}CuO_{4-\delta} > La_{0.8}Sr_{0.2}MnO_{3-\delta} > La_{0.8}Sr_{0.2}CrO_{3-\delta} \approx La_{0.8}Sr_{0.2}YO_{3-\delta}$. The activity of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ was compared with supported Pd, Pt and also with unsubstituted $LaCoO_3$ catalysts under similar reaction conditions. Among all the catalysts tested in this study, Pd/Al_2O_3 showed the lowest light-off temperature for N_2O decomposition. The activity of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ was found to be comparable to Pd/Al_2O_3 catalyst at temperatures above 500°C. The influence of added oxygen (about 4%) in the feed was examined over $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ and Pd/Al_2O_3 catalysts and only in the case of cobalt catalyst was the conversion of N_2O decreased by $\sim$ 13%. By choosing varied sintering conditions, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ of different BET surface areas were prepared and the light-off temperature was found to decrease with increase in surface area. The results obtained over solid solutions are discussed on the basis of the cation mixed valency and oxygen properties of the catalyst.

Keywords: solid oxide solutions; perovskite type oxides; supported noble metals; nitrous oxide decomposition

1. Introduction

The decomposition of N_2O into its elements has been one of the best model reactions to evaluate the catalytic activity of many materials in heterogeneous catalysis. Details on the kinetics and mechanism of the reaction on metals and metal oxide catalysts are reported extensively in the literature [1–3]. Considerable effort has

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been made in recent years on the commercial feasibility study of nitrous oxide decomposition as a means of treating the by-product exit gases in many combustion reactions [4–6]. Studies related to the reduction of NOx in the exhaust gas treatment revealed that, in many cases, nitrous oxide has been the major undesired by-product in the reaction [7]. Mixed oxides with perovskite type structure have been suggested for many applications such as superconductors, electrode materials and catalysts for oxidation–reduction processes [8–10]. Swamy et al. have recently reviewed the decomposition of N_2O over perovskite related oxides and the electronic theory in N_2O catalysis has been mostly addressed by exhibiting various correlations between the physicochemical properties of the catalyst and the catalytic activity [3].

Zeolite based catalysts have also been widely tested for N_2O decomposition [11–15]. Li et al. [15] have reported a wide range of zeolite based catalysts to show a promising catalytic activity for N_2O decomposition in the temperature range of 250–400°C. Copper and cobalt exchanged ZSM5 were found to be more active than the other cation exchanged zeolites. There was higher reaction rate (2.7×10^{-3} mol/g h) than those of the other zeolitic catalyst systems, which exhibited reaction rates of 1×10^{-4} to 1×10^{-7} mol/g h.

In our previous communications, we reported the catalytic activity of $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Cr, Fe, Mn, Co or Y) compounds for oxidation and hydrogenation reactions [16–19]. The activity for CO oxidation of the solid solutions of $La_{1-x}Sr_xCrO_3$ was very similar to that of Pt/Al_2O_3 catalyst, while for propylene hydrogenation reaction, the Cr SOS and Pt catalysts exhibit a similar kinetic behavior (simple Langmuir–Hinshelwood).

In the wake of our earlier studies, the present work has been focused on the $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Cr, Fe, Mn, Co or Y) and $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ oxides for the decomposition of N_2O, which has not been previously reported under the present reaction conditions. Supported Pt and Pd catalysts have been considered in this study to obtain a comparison with the mixed oxide systems. Therefore, the objectives of the present study are: (i) to compare the nitrous oxide decomposition activity of various Sr substituted perovskite related oxides $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Cr, Fe, Mn, Co or Y) and $La_{1.8}Sr_{0.2}CuO_{4-\delta}$, (ii) the mixed oxide catalytic activity with that of some selected supported noble metal catalyst (Pt and Pd), (iii) to study the influence of added oxygen on the decomposition reaction and (iv) to examine the influence of surface area on the N_2O decomposition over $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ catalyst.

2. Experimental

The solid oxide solution (SOS) catalysts $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Cr, Fe, Mn, Co or Y) and $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ were all prepared by the Pechini process. The details have been described elsewhere [17]. The chemicals used for the preparation of catalysts (lanthanum nitrate, strontium nitrate, transition metal nitrates, citric acid and ethylene glycol) were, at least 99.9% purity, obtained from either Aldrich chemicals or Johnson Matthey, USA. The resultant oxides were subjected to different calcination schedules to obtain oxides with perovskite structure.

The supported noble metal catalysts, Pd(0.5%)/Al_2O_3, Pd(0.5%)/carbon and Pt(0.5%)/Al_2O_3 were supplied by Engelhard Industries Division, New Jersey, USA.

X-ray diffraction studies were performed on all oxide catalysts using Diano 8535D automatic X-ray diffractometer with Cu K_α radiation and scan rate of 1°/min. The surface area of all the samples were measured with Quantachrome single point BET surface area analyzer (Monosorb MS-16) using 30% nitrogen in helium gas mixture.

The catalytic decomposition of nitrous oxide was carried out in a gradientless recycle reactor operated at 1 atm pressure [20]. A feed containing 0.5% nitrous oxide and balance helium was used in all experiments. Studies were also made with 4% oxygen in the feed gas on selected catalyst systems. A total constant flow rate of about 100 ± 2 cm^3/min and recycle ratio of 30 were maintained in each catalytic run. The reactor gas composition was analyzed at regular equilibrated temperature intervals by an on-line gas chromatograph. The activity of all catalysts was obtained from the fraction of nitrous oxide converted as a function of temperature in the range 25–600°C. Each measurement was made at constant temperature under steady state conditions.

The catalytic activity of N_2O decomposition in the present study is represented as the light-off temperature (LOT) curves, where LOT is the temperature of the reaction initiation. The LOT curves are then constructed with the conversion of N_2O as a function of reaction temperature.

A blank experiment was conducted without the catalyst powder (up to 700°C) to ensure the absence of thermal reaction under the present experimental conditions. compressed gas tanks of nitrous oxide, oxygen and helium (99.9% purity) were all supplied by Mittler supply Inc, South Bend. Nitrous oxide was used as obtained without any further purification.

3. Results and discussion

X-ray powder diffraction analysis confirmed all the mixed oxides to possess the desired single phase perovskite structure and the *d*-spacings were compared with the data of the unsubstituted parent perovskite compounds. The oxide $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ sintered at 700°C also indicated the peaks corresponding to the perovskite phase only. This conforms with our previous reports that some of these solid solutions crystallize in perovskite structure at low temperatures [19]. Based on our early study, the Cr and Y solid oxide solutions were prepared by sintering at 1050°C. The Cr compound prepared below 1000°C was green in color with low activity for CO oxidation while high activity was observed with the black chromite sintered at 1050°C [19]. The X-ray diffraction analysis showed that the yttrium perovskite could be prepared only above 1000°C. The BET surface areas of the SOS are found to be in the range 1–12 m^2/g which are many orders lower than for the supported metal catalysts. It is known that the overall composition and preparation condition of the catalysts generally determine the resulting surface area and therefore, the values of the solid solutions are not uncommon (table 1). The various physicochemical properties of the catalysts used in the present study are listed in table 1.

The light-off temperature (LOT) curves for the conversion of nitrous oxide as a function of temperature over $La_{0.8}Sr_{0.2}MO_{3-\delta}$ oxides are shown in fig. 1. These solid solution catalysts show activity for the decomposition reaction at temperatures above 300°C. It can be seen from fig. 1 that Co and Fe in the SOS series exhibit a promising performance for the N_2O decomposition with conversion of about 55 and 32% respectively at 500°C. The Co perovskite has been reported to exhibit the highest activity even in the unsubstituted $LaMO_3$ (M = Cr, Mn, Fe or Co) series [21]. $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ and $La_{0.8}Sr_{0.2}YO_{3-\delta}$ catalysts did not show any conversion of nitrous oxide up to 500°C which were excellent candidates for CO oxidation and CH_4 oxidation respectively [18].

The activity (LOT curves) of the supported noble metals tested in the present study for N_2O decomposition is shown in fig. 2. Among the noble metal catalysts, Pd/Al_2O_3 showed the highest activity with 79% conversion at 500°C compared to 25 and 18% for the other two catalysts (Pt/Al_2O_3 and Pd/C respectively). The results observed with Pd/Al_2O_3 and Pt/Al_2O_3 in the present study are consistent with those reported by Li et al. [15]. The global rate (R_g) of the reaction was computed using the following equation, applicable to a recycle reactor operating under CSTR conditions (i.e. recycle ratio greater than 25):

Table 1
Physicochemical and catalytic properties of various catalysts tested for nitrous oxide decomposition reaction [a]

Catalyst	Sintering temp. (°C)	Conduction type	Surface area (m^2/g)	Catalyst weight (g)	Conversion at 500°C (%)	Global rate (R_g) (mol/m^2 s)	E_a (kcal/mol)
Pt/Al_2O_3	–	metallic	249.0	0.125	25.8	2.49×10^{-9}	17.9
Pd/Al_2O_3	–	metallic	102.5	0.128	79.1	1.91×10^{-9}	13.5
Pd/C	–	metallic	560.5	0.128	18.0	8.93×10^{-9}	10.6
$La_{1.8}Sr_{0.2}CuO_4$	1000	p-type	2.2	0.3052	12.2	5.69×10^{-8}	37.2
$La_{0.8}Sr_{0.2}CrO_3$	1050	p-type	1.1	0.232	0.5	1.19×10^{-9}	31.6
$La_{0.8}Sr_{0.2}MnO_3$	1000	p-type	2.7	0.265	8.3	4.44×10^{-8}	34.4
$La_{0.8}Sr_{0.2}YO_3$	1050	electrolyte	1.2	0.229	0.5	1.40×10^{-8}	40.4
$La_{0.8}Sr_{0.2}FeO_3$	1000	p-type	2.6	0.268	32.0	1.42×10^{-7}	25.9
$La_{0.8}Sr_{0.2}CoO_3$	700	p-type	11.4	0.253	72.2	6.04×10^{-8}	11.3
$La_{0.8}Sr_{0.2}CoO_3$	850	p-type	5.8	0.275	68.2	1.43×10^{-7}	–
$La_{0.8}Sr_{0.2}CoO_3$	1000	p-type	2.1	0.274	55.5	3.24×10^{-7}	–
$LaCoO_3$	850	p-type	6.6	0.277	40.5	7.88×10^{-8}	35.2

[a] Feed composition: 0.5% N_2O in helium; feed flow: 100 ± 2 cm^3/min; recycle ratio: 30.

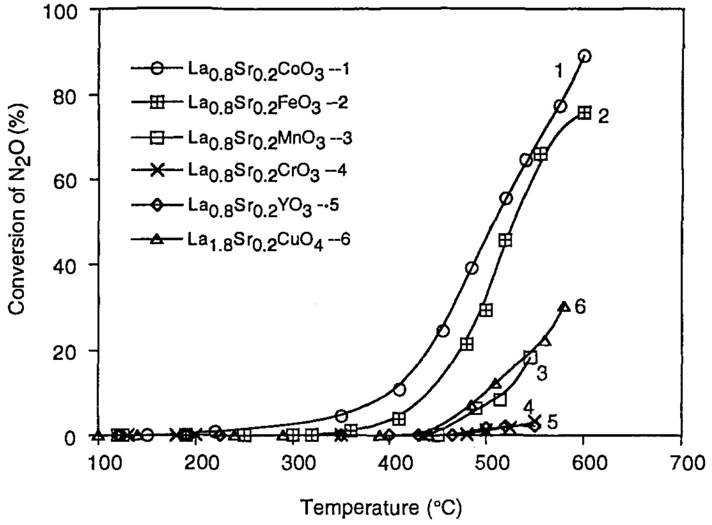

Fig. 1. Light-off temperature curves for the nitrous oxide decomposition over various solid solutions, $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Co, Fe, Mn, Cr or Y) and $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. Catalyst weight ≈ 0.25 g. N_2O concentration= 0.5%; total flow rate = 100 ± 2 cm^3/min.

$$\text{global rate } (R_g) = C_f\chi/\theta\,,$$

where C_f = concentration of nitrous oxide in the input feed (mol/cm^3), χ = fraction of nitrous oxide converted at a given temperature and θ = residence time

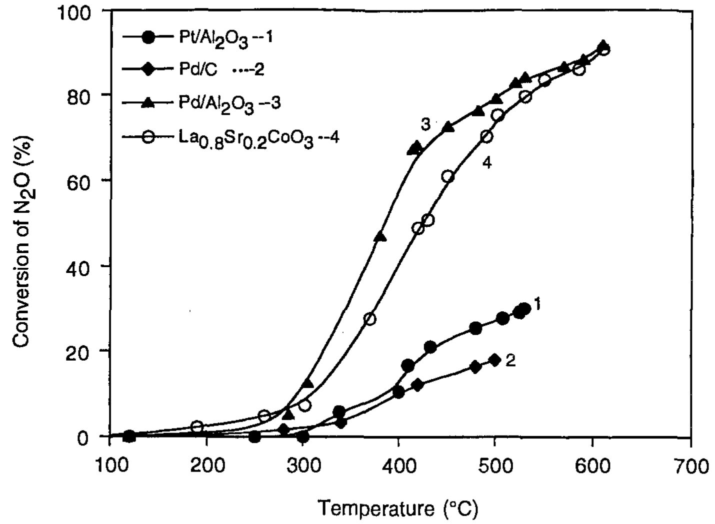

Fig. 2. Comparison of light-off temperature curves for the nitrous oxide decomposition between supported noble metal and $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ catalysts. N_2O concentration = 0.5%; total flow rate = 100 ± 2 cm^3/min. Catalyst weight ≈ 0.125 g for noble metals and 0.25 g for Co SOS. The data of Co SOS corresponds to the sample sintered at 700°C with surface area of 11 m^2/g.

(weight of the catalyst over total volumetric flow rate of reactant). The N_2O conversion at 500°C and the corresponding global rate are listed in table 1. The apparent activation energies (E_a) were computed at conversions below 10% on all the catalysts and the Arrhenius plots are compared in fig. 3. The E_a values of 13.5 and 18 kcal/mol are obtained for Pd/Al_2O_3 and Pt/Al_2O_3 respectively. For most of the SOS the E_a values are quite high (30–40 kcal/mol) except for the Co solid solution (11.3 kcal/mol). This range of values have been noted in the case of metal oxide catalysts [2]. To compare the activity of noble metal with that of SOS, the LOT of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (sample sintered at 700°C with surface area of 11 m^2/g) is included in fig. 2. The difference in the conversion of nitrous oxide between SOS and noble metal is significant at reaction temperatures below 500°C. However, at higher temperatures of about 600°C the activities of both the catalysts approach each other. One reason for this behavior may be the influence of product oxygen in the reaction which has been well established in the N_2O decomposition reaction over various catalysts [3,20]. It should also be noted that the surface areas of the supported Pd and Pt catalysts are many orders of magnitude higher than those of the solid oxide solutions.

To obtain more information on the oxygen effect, experiments were conducted with feed containing 4% added oxygen with Pd/Al_2O_3 and $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ catalyst and the results are shown in table 2. Note that the conversion of nitrous oxide decreased by about 13% with the SOS, which could be due to the competition between N_2O and O_2 for the adsorption sites on the surface. The results of Pd/Al_2O_3 are similar to that observed over Pd filaments by Redmond [1].

The $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ SOS catalyst offered the most promise with activity com-

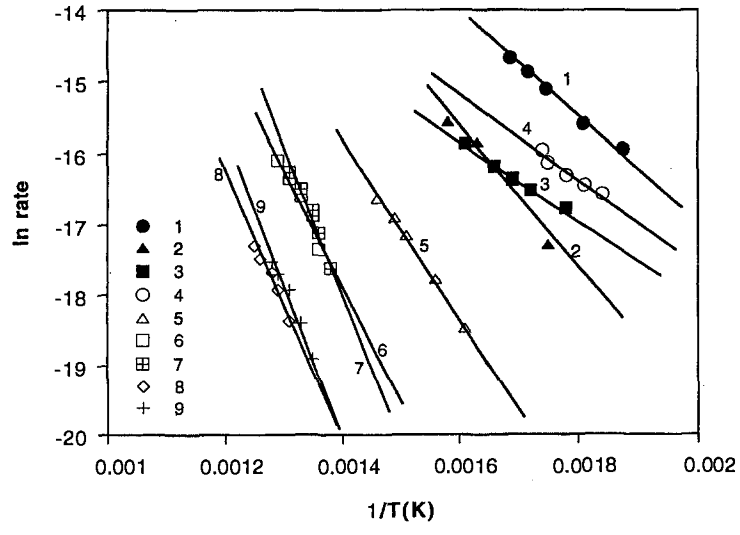

Fig. 3. Comparison of Arrhenius plots for the decomposition of nitrous oxide over different catalysts. (1) Pd/Al_2O_3, (2) Pt/Al_2O_3, (3) Pd/C, (4) $La_{0.8}Sr_{0.2}CoO_3$, (5) $La_{0.8}Sr_{0.2}FeO_3$, (6) $La_{0.08}Sr_{0.2}MnO_3$, (7) $La_{1.8}Sr_{0.2}CuO_4$, (8) $La_{0.8}Sr_{0.2}CrO_3$ and $La_{0.8}Sr_{0.2}YO_3$.

Table 2
Comparison of activity for nitrous oxide decomposition with and without added oxygen on different catalysts [a]

Catalyst	N_2O conc. (%)	Conversion at 500°C (%)	global rate (R_g) (mol/m^2 s)	Ref.
Pd/Al_2O_3	0.452	79.1	8.93×10^{-9}	this work
Pd/Al_2O_3 [b]	0.51	78.5	8.51×10^{-9}	this work
$La_{0.8}Sr_{0.2}CoO_3$	0.409	74.8	6.04×10^{-8}	this work
$La_{0.8}Sr_{0.2}CoO_3$ [b]	0.422	62.0	9.85×10^{-9}	this work
Pd/Al_2O_3	0.099	85.0	6.51×10^{-7}	[15]
Pt/ZSM5	0.099	20.0	1.8×10^{-8}	[15]
$LaCoO_3$	0.409	57.8	6.88×10^{-7}	this work
$La_{1.75}Sr_{0.25}NiO_4$	20.0	– [c]	3.1×10^{-5}	[29]

[a] Feed composition: 0.5% N_2O + balance helium; feed flow: 100 ± 2 cm^3/min; recycle ratio: 30.
[b] Data corresponds to 4.2% oxygen in the feed.
[c] – Data not available.

parable to Pd if large surface area powders could be prepared. By sintering at lower temperatures (700 and 850°C for 6 h) SOS catalysts with surface area of 11.0 and 6 m^2/g respectively were produced. The N_2O decomposition results on these catalysts as well as on the unsubstituted $LaCoO_3$ are shown in fig. 4. As shown in fig. 4 the LOT for 50% N_2O conversion was found to decrease from 510 to 430°C (i.e. activity increase) with an increase in the surface area of 2 to 11 m^2/g respectively. Similar effect of increased activity with high surface area has been reported

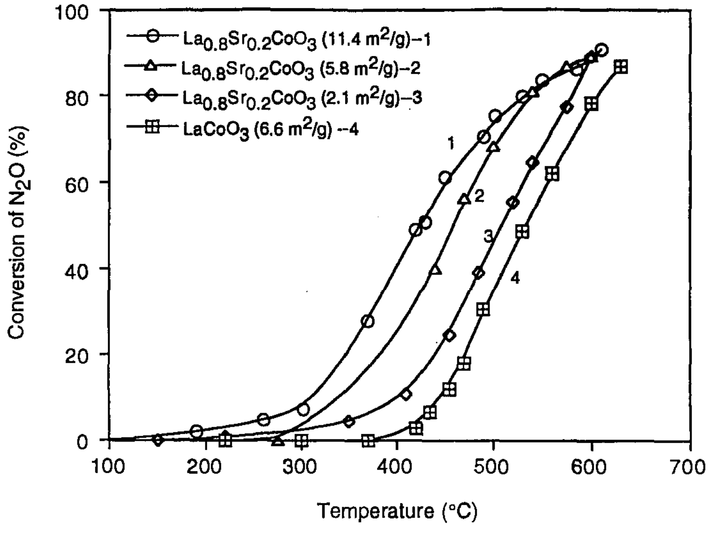

Fig. 4. The influence of surface area on the decomposition of nitrous oxide over $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (surface area values are given in parentheses). Catalyst weight ≈ 0.25 g. N_2O concentration = 0.5%; total flow rate = 100 ± 2 cm^3/min.

in the case of methane conversion, CO oxidation and propane oxidation reactions over perovskite type mixed oxides [24–26].

It is well known that with ABO_3 type perovskites, the B-ions mainly contribute the catalytically active sites and the A-ions are generally inert or play a modifying role [3,21]. The results presented in fig. 1 for the $La_{0.8}Sr_{0.2}MO_{3-\delta}$ series clearly indicate the significance of the nature of B-ion on the N_2O decomposition. The partial substitution of Sr^{2+} on the La^{3+} sites in $LaMO_3$ system can lead to either the formation of oxide ion vacancies or the formation of M^{4+} (electron holes) in order to maintain the electrical neutrality. It is known that in yttrium SOS ($La_{0.8}Sr_{0.2}YO_{3-\delta}$) the Sr doping results only in the formation of oxide ion vacancy with $\delta = 0.1$ [25]. It has also been reported to exhibit a mixed conducting type behavior (p-type and electrolyte/ionic) at ambient atmosphere. At low partial pressure of oxygen ($< 10^{-6}$ atm) an ionic conductivity predominates over the electronic conductivity. In $La_{0.8}Sr_{0.2}CrO_{3-\delta}$, δ was found to be zero even at low partial pressure of oxygen (10^{-11} atm) and essentially showed high p-type electrical conductivity [17]. Both these (Cr and Y SOS) catalysts exhibit a very low N_2O conversion of 3–4% and therefore either the oxygen vacancy concentration or purely electronic conductivity (p-type) alone is not an important factor in N_2O decomposition. The other members in the present SOS series can exist in both M^{4+} and oxide ion vacancy state for the corresponding doping of Sr at lanthanum sites. These oxides showed promising activity indicating that multiple oxidation state of the B-ion combined with oxygen vacancy form active catalysts.

3.1. MECHANISTIC INFERENCES

The mechanism of nitrous oxide decomposition on various metal oxide catalysts has been well documented in the literature [1–3]. The key elementary steps involved in the decomposition reaction can be summarized as follows:

$$N_2O(g) \rightleftharpoons N_2O(a) \tag{1}$$

$$N_2O(a) \rightarrow N_2(g) + O^-_{(a)} \tag{2}$$

$$2O^-_{(a)} \rightleftharpoons O_2(g) \tag{3}$$

$$O^-_{(a)} + N_2O(g) \rightarrow N_2(g) + O_2(g) \tag{4}$$

The importance of product oxygen in the decomposition reaction has been well understood and the desorption of oxygen has been found to be the rate controlling step in the overall process. However, at low N_2O concentrations (<50 Torr) eq. (1) was shown to be the rate determining step on oxide catalysts [26]. Among the semiconducting oxides, the p-type oxides have been reported to show a higher N_2O activity than either n-type or insulators [27]. Studies on the reduction–oxidation properties as well as nonstoichiometry and desorptivity of oxygen over $La_{1-x}Sr_xMO_{3-\delta}$ (M = Co, Fe or Mn) indicate the operation of a redox mechanism for the oxidation reaction [22,28,29]. With respect to redox properties, the oxygen desorption process may well be a predominant factor in the observed activity over Co solid solution. The effect of added oxygen in the reaction feed also supports the above conclusion (table 2). A similar situation has been noted in the case of $LaCoO_3$ catalyst with 50 and 200 Torr concentrations of nitrous oxide [30]. However, more detailed kinetic studies are warranted to explain the observed trend in the activity on these catalysts.

3.2. SOS vs Pd/Pt ACTIVITIES

The activity of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ is compared with the supported Pd and Pt catalysts in fig. 2. It is interesting to observe that similar N_2O activity was realized for the Co perovskite and Pd catalyst at temperatures above 500°C. The activity of the cobalt based catalysts tends to approach the same conversion limit at temperatures near 600°C. This could possibly be due to the enhanced mobility of SOS oxygen both in the surface and bulk at high temperatures.

The Co in Co/ZSM5 catalyst did not reveal any decrease in the conversion of N_2O with the added oxygen (2.5%) in the N_2O feed [15]. The low activity of Pt/Al_2O_3 catalyst may be explained on the basis of the strong inhibition of the product oxygen with the Pt site making the desorption of oxygen less facile. Pt supported on ZSM5 catalyst has also been reported to show very low activity (20% conversion at 500°C) [15].

4. Conclusions

Among the solid oxide solution (SOS) catalysts, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ was found to have the highest activity for N_2O decomposition. Pd/Al_2O_3 showed the lowest light-off temperature (highest activity) of the supported noble metal catalysts as well of all catalysts employed in the present study. The activities of Co solid solution (SOS) and Pd catalysts are found to be comparable at temperatures above 500°C. The addition of oxygen to the feed is found to decrease the conversion of N_2O by 10% only on SOS as no effect was seen over Pd/Al_2O_3. The LOT of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ was found to decrease by 80°C (i.e. activity increase) with surface area increase of 2 to 11 m^2/g.

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