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Catalytic Decomposition of Nitric Oxide by Perovskites

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Abstract–Catalytic decomposition of nitric oxide has been studied for nearly a century, using materials ranging from noble metals to alkaline earth metal oxides, without much success. Only since about last fifteen years some progress in finding promising materials has been made. Of the numerous catalyst systems studied, very few show tangible decomposition rates : copper substituted zeolites, silver-cobalt mixed oxides, some perovskites, and supported noble metals. Although at 773 K the rates of decomposition over zeolites are two to three orders higher than those over remaining systems, these materials have very low thermal stability, above 773 K. In this respect, perovskites have much higher potential, although so far no composition exhibiting practical decomposition rates has been found. Systematic study of the effect of composition on the performance should help to advance the complete understanding of this important reaction. In this paper a current state of art is outlined, and some latest preliminary results for new specially formulated perovskites are presented.

Key words : Nitric Oxide Catalytic Decomposition, Perovskites, Nitric Oxide Removal Treatments

INTRODUCTION

Nitrogen oxides, NO_x (NO_x comprising a noxious nitrogen dioxide NO_2, and nitric oxide NO), have been recognised as one of the major and most serious pollutants for many years [Hightower and van Leisburg, 1975]. Due to their implication in photochemical smog formation, acidic depositions, stratospheric ozone depletion, and global warming abatement of these NO_x emissions and eventually their elimination is increasingly urgent.

Most of the NO_x are the consequence of nitric oxide formation during the high temperature combustion of coal, oil or natural gas, or potentially hydrogen, in power plants, and of automotive fuels in internal combustion engines. The third largest source are natural gas-fuelled turbines. When released to atmosphere, nitric oxide oxidises at low temperatures to lethal nitrogen dioxide (NO_2).

NO_x emissions from the manufacture of nitric acid and from its use in the production of a variety of organic chemicals and from other industries represent only a small portion (~3 %) of total, but their concentrations at the point of emission are much larger than from combustion. These chemical industry emissions are often accompanied by high concentrations of sulfur dioxide and therefore require special abatement treatment for their removal.

Nitrous oxide (N_2O) is not a direct health hazard (it is not included in NO_x species) and is generated in quantities of less than about 5 % of the total nitrogen oxides emissions, either by chemical processes (for example from adipic acid manufacture) or during combustion [Hulgaard and Dam-Johansen, 1993]. However, concerns about its release into atmosphere are growing because it is a greenhouse gas and a source of stratospheric NO. Small quantities of nitrous oxide may also result from an incomplete nitric oxide reduction.

The NO_x emissions are being controlled by both clean and cleanup technologies. In the area of combustion, the clean technologies include the use of nitrogen free fuels, but are mostly based on the reduction of the combustion temperature through a variety of means such as better design and precise control of the fuel/air ratio [Gard, 1994; Kuehn, 1994], or catalytic combustion. Catalytic combustion holds the best promise as the most efficient [Prasad et al., 1984; Trimm, 1984; Pfefferle and Pfefferle, 1987; Arai and Machida, 1991]. Nevertheless, since the formation of nitrogen oxides can hardly be totally prevented, development of secondary, postcombustion treatment technologies is equally important. Currently available clean-up technologies [Wood, 1994] cover a variety of NO_x removal processes (post-combustion treatments) which include wet or dry scrubbing and catalytic reduction [Cho, 1994; Shelef, 1995]. While many of the cleanup technologies have proven efficient each has its limitations and general consensus exists that development of catalytic NO decomposition to nitrogen and oxygen at mild temperatures in the presence of oxygen is highly desirable.

Although nitric oxide is not at low temperatures thermodynamically stable, its decomposition is so slow that it needs acceleration by either an external energy (radiation) source or by efficient catalysts.

Catalytic decomposition of nitrogen oxides, in particular of nitric oxide, has been studied for nearly a century. In the mid sixties, as part of the effort to clean the automotive effluents, this area of research was very intensive [Hightower and van Leirsburg, 1975] and many materials covering a wide range of simple or complex metal oxides from alkaline earth to transition metal oxides and supported noble metals have been tested

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for their activity [Shelef and Ganghi, 1969; Winter, 1971; Amirnazmi et al., 1973; Meubus, 1977; Golodets, 1983]. Studies of some perovskite catalysts, principally cobaltates and manganites were part of this early effort [Chien et al., 1975; Voorhoeve et al., 1975]. Of these previously studied materials supported platinum and low temperature cobalt oxide spinel, Co_3O_4, showed the highest activities but even these were several orders lower than required for practical use [Hightower and van Leirsburg, 1975]. Thus deemed impractical, although its general appeal has not been abandoned completely, catalytic nitric oxide decomposition had to be replaced by catalytic reduction systems. Nevertheless, over the last decade we are witnessing renewed interest in this important area of catalysis which seems to intensify as new important information and knowledge are gained. This renewal has apparently been triggered by the discovery that some copper-ZSM zeolites exhibit substantially superior activity for nitric oxide decomposition than any other known material [Iwamoto et al., 1981, 1991]. While the interest in transition metal, particularly copper, exchanged zeolites has been growing [Li and Hall, 1991; Hall and Valyon, 1992; Shelef, 1995; Iwamoto, 1996; Bell, 1997], other materials, such as silver doped cobalt oxides [Hamada et al., 1990], or new perovskite compositions [Shimada et al., 1988; Tabata et al., 1988; Teraoka et al., 1990; Tabata and Misono, 1990; Yasuda et al., 1990, 1993] have been searched and developed. Although by the early nineties only copper zeolites, doped cobalt oxide Co_3O_4, perovskites, and supported noble metals were considered as the promising materials [Iwamoto and Hamada, 1991; Iwamoto and Yahiro, 1994], several laboratories are reinvestigating some simple oxides which were previously found unpromising. Among these are rare earth oxides [Zhang et al., 1995; Vannice et al., 1996], manganese oxides [Yamashita and Vannice, 1996, 1997], copper-chromic oxide [Lee et al., 1996], and supported barium oxide [Xie et al., 1997]. Platinum group metals also continue to attract attention [Ogata et al., 1993; Chuang and Tan, 1997]. All this most recent research activity is apparently directed towards providing a better understanding of this elusive nitric oxide decomposition reaction system. This in turn could lead to the development of a truly performing practical catalyst. Such catalyst has to provide a fast nitric oxide decomposition, and has to be thermally stable in the atmosphere of not only up to nearly 10 % oxygen, but also up to 9 % carbon dioxide and up to 18 % water vapor. The suitable catalyst must also be insensitive to poisoning by sulfur oxides.

In spite of their high catalytic activity zeolites, similarly as the silver promoted cobalt oxides have a limited thermal stability and are very easily poisoned. For this reason their future practical application remains highly uncertain. With respect to much better thermal stability, extending to nearly 1,100 K, and good resistance to sulfur poisoning noble metals still deserve some attention. There may be ways of improving their performance [Chuang and Tan, 1997].

Similarly, some perovskites, the structurally unique mixed oxides represented by the general formula $ABO_{3-\delta}$ have a relatively good thermal stability and some may be reasonably well resistant to sulfur poisoning [Klvana et al., 1997a, b].

In general, it is believed that perovskite structure provides the widest range of possibilities to tailor characteristic properties required for high activity towards nitric oxide decomposition. Of these large number of suitable adsorption sites which may include different surface oxygen species, high electron mobility, high oxygen ion mobility, as well as an easy oxygen desorption may be considered as the most important. Having already acquired a good experience with perovskite catalysts we are extending our interest to the nitric oxide decomposition, and will now concentrate on this group of materials. Nevertheless, before presenting a short review of the available work involving perovskites, a brief outline of the currently available knowledge concerning the kinetics and mechanism of the catalytic nitric oxide decomposition is given first.

1. Kinetics and Mechanism of Nitric Oxide Decomposition

In principle same working model should be applicable in general, although relative importance of various elementary steps in the mechanism are certainly function of the catalyst. Following are the most important steps :

(1) Adsorption of the nitric oxide molecule.
(2) Pairing of two nitrogen oxide species at the catalyst surface.
(3) Surface decomposition of the dinitrogen species to liberate gas phase dinitrogen.
(4) Surface held oxygen desorption.

All studies in which the effect of oxygen on the activity has been included in the experiments indicated that the presence of oxygen decreases the activity. Thus, slow desorption of oxygen has been considered either as a controlling, or at least competing step in the overall reaction scheme, and was taken into account in the various rate equations [Winter, 1971; Amirnazmi et al., 1973; Teraoka et al., 1993; Li and Hall, 1991]. Furthermore, based on the fact that oxidizable transition metal oxides showed higher activity than other oxides forming strong metal-oxygen bonds, it has been generally accepted that the overall mechanism involves a redox cycle in which the reactant (NO) is the oxidant, and the desorbing oxygen acts as the reductant of the activation sites of the catalyst. This view has been further strengthened by the fact that on accepting an electron, the nitrogen-oxygen bond in the resulting NO^- ion is weakened, and that the highly active catalysts, whether zeolites [Iwamoto et al., 1976; Valyon and Hall, 1993a] or some perovskites [Teraoka et al., 1990] can reversibly adsorb and desorb large quantities of oxygen.

In spite of the existing strong arguments in favor of the redox type mechanism adopted initially even for copper zeolites [Li and Hall, 1991; Hall and Valyon, 1992; Valyon and Hall, 1993a], Shelef, using thermodynamics for his reasoning has presented an alternative scheme [1992, 1995] later supported by experiments [Kucherov et al., 1994]. This alternative mechanism, now apparently accepted also by Valyon and Hall [1993b], involves a formation of an adsorbed $-NO_2$ intermediate on the active Cu^{2+} site. Both mechanism can be used to derive the same rate equation. While the question of the correct mechanism is still not entirely settled, in particular the role of oxygen, the most recent very significant work from the Lungsford's laboratory on the activity of supported barium oxide [Xie et al., 1997] is strongly in favor of the latter non-redox mechanism. Not only did Xie et al., show a previously unknown relatively high activity of barium oxide, but they were also able to trace by raman spectroscopy the nitrogen bound $-NO_2$ species as the intermediate (precursor) of this high activity. Surprisingly, Xie et al., have not compared their proposed reaction scheme with that of Shelef's, but in view of the ability of cupric ion to form peroxide, similarly as barium does, the linkage between the two proposed mechanisms seems very tempting.

While the new findings have to be taken into consideration, for the case of perovskites the properties already outlined as leading to high activity may still remain important.

2. Perovskites in Nitric Oxide Decomposition

The early studies involving cobalt and manganese based perovskites have shown activities too low for practical use, in addition to their high sensitivity to sulfur poisoning [Chien et al., 1975; Voorhoeve et al., 1975] and the interest in these materials has faded for some time. In 1979 Shin et al., have reported a relatively interesting, although still impractical, rates observed over strontium ferate. Based on infrared spectroscopic study, Shin et al. [1979b] concluded that NO adsorbs on $SrFeO_{3-x}$ as a nitrosyl ion (NO^-) considering it as a precursor for the cleavage of the N-O bond. Some ten years later a new interest in perovskite-type catalysts has apparently been inspired by the discovery of "high" temperature superconductivity in $YBa_2Cu_3O_{7-\delta}$ and several interesting reports appeared in the literature. One of the seemingly most attractive was by Tabata in 1988, who monitoring the NO concentration only, hastily reported high conversions of 51 ppm NO in the presence of 8.1 % oxygen over $YBa_2Cu_3O_{7-\delta}$ at 600 K. However, it was later shown by Tabata et al. [1988] and by Arakawa and Adagi [1989] that at temperatures between 500 to 800 K NO adsorbs and desorbs reversibly, with only a small fraction of NO being decomposed to the elements. The fast decomposition was found to take place at much higher temperatures [Shimada et al., 1988]. These materials have also been studied by Hallasz et al. [1991, 1993]. Other cuprates, in particularly those with a K_2NiF_4 structure have been studied by Yasuda et al. [1990, 1993] without much improvement in activity. However, Yasuda et al. [1993] were able to show in full detail that oxygen desorption is not the rate-determining step over these catalysts. A more systematic study of several different perovskite multi transition metal compositions by Teraoka et al. [1990, 1993] has indicated that improvement in activity can be obtained with a careful composition design, and to a smaller degree by increasing the specific surface area. For example Shimada et al. [1988] attempted, more or less successfully, to increase the surface area of $YBa_2Cu_3O_{7-\delta}$ by supporting it on magnesium oxide. Yet, for practical applications, the activities were still much to low. Nevertheless, the interest in perovskite type materials continues [Yokomichi et al., 1996; Zhao et al., 1996; Yokoi and Uchida, 1997] and entirely new compositions are being added to the list [Mori and Yamamura, 1994; Bontchev et al., 1996].

In our opinion, the perovskite compositions tested so far for NO decomposition have not been sufficiently well representative of the basic requirements for high activity. We believe that improvement could be obtained by selecting the right composition, and by increasing the specific surface area through appropriate preparation method. In the next section the preliminary results of our study are presented.

DEVELOPMENT OF NEW NITRIC OXIDE DECOMPOSITION PEROVSKITE CATALYSTS

Our previous studies have shown that oxygen deficient electrically conducting nickel-cobalt based perovskites exhibit excellent activity not only as electrocatalysts [Kirchnerova and Klvana, 1994], but also as combustion catalysts [Kirchnerova et al., 1993; Klvana et al., 1994]. In addition, these perovskites have a reasonably good resistance to sulfur poisoning and are thermally stable to at least 1,000 K [Klvana et al., 1997a, b]. Furthermore, similarly as a number of other oxygen deficient perovskites, our nickel-cobalt based compositions also exhibit a high capacity to sorb reversibly relatively large amount of oxygen. It was therefore of interest to attempt to design new compositions in a way to maximize their performance in the nitric oxide decomposition. To satisfy the requirement of potentially easy oxygen desorption, as well as sufficient number of electron donor sites, we have targeted compositions containing nickel and copper. The complementary B-site ions were then selected in a way to assure a good stability of the perovskite structure to at least 1,000 K. Such perovskites are relatively difficult to synthesize, but with a careful attention to the method of preparation, we have succeeded to produce several new perovskite compositions as indicated in Table 1.

1. Catalyst Preparation and Characterization

All samples were prepared by a method based on freeze-drying a slurry of precursor components comprising reactive hydroxides and dissolved metal nitrates [Kirchnerova and Klvana 1998]. This precursor slurry was obtained by suspending lanthanum hydroxide in a solution of metal nitrates. All components were mixed in a strictly stoichiometric proportions. The least amount of water necessary to dissolve all nitrates and to give a fluid, but sufficiently stable for further processing, suspension was used. The suspension was quickly frozen by spraying or by direct pouring in liquid nitrogen, the frozen material separated from the nitrogen, and then dried under vacuum. The freeze-dried precursor powder mixture was calcined in air under controlled conditions, typically 12 h at 863 K followed 4 h at 923 K.

Formation of the perovskite phase was confirmed by X-ray powder diffraction on a Philips X'Pert diffractometer using Cu-

Table 1. Composition and characteristics of perovskites studied in NO decomposition

Composition	I.D.	d	SSA m^2/g
$La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_{3-\delta}$	LSNC	0.17	9.0
$La_{0.66}Sr_{0.34}Ni_{0.29}Co_{0.69}Fe_{0.02}O_{3-\delta}$	LSNCF	0.17	10.5
$La_{0.4}Sr_{0.6}Mn_{0.4}Ni_{0.6}O_{3-\delta}$	LSMN-46	< 0.3	16.0
$La_{0.7}Sr_{0.3}Mn_{0.3}Ni_{0.7}O_{3-\delta}$	LSMN-37	0.15	9.8
$La_{0.87}Sr_{0.13}Mn_{0.2}Ni_{0.8}O_{3-\delta}$	LSMN-28	> 0.065	12.7
$La_{0.95}Sr_{0.05}Mn_{0.17}Ni_{0.83}O_{3-\delta}$	LSMN-19	> 0.025	10.5
$La_{0.8}Sr_{0.2}Cu_{0.15}Fe_{0.85}O_{3-\delta}$	LSCuF	< 0.175	10.1
$La_{0.8}Sr_{0.2}Cu_{0.15}Al_{0.85}O_{3-\delta}$	LSCuA	0.175	21.8
$La_2CuO_3/CuO/LaFeO_3$	LFCu		8.6

α irradiation.

Specific surface area (SSA) of the powders was determined by a single-point BET method on a Micromeritics Flow Sorb II 2300 apparatus with nitrogen as the adsorbate, using the gas mixture of 30 % nitrogen in helium.

2. Catalyst Performance Evaluation

Performance of catalyst samples was evaluated at ambient pressure in an integral stainless steel U-type reactor, similarly as was the case of combustion catalysts [Klvana et al., 1994]. The reactor having 0.7 cm inner diameter, 10 mL reaction zone, 30 cm overall length was loaded with the catalyst fine powder (1 or 1.5 g) mixed with inert pumice particles (250-500 μm) to approximate isothermicity. Before starting the evaluation, the reactor was first purged several hours at 773 K by pure helium to remove air and adsorbed impurities. FTIR analyzer was used to detect impurities. For measurements the reactor was heated in intervals of 50 degrees. When a stable temperature was obtained, the conversions of nitric oxide to nitrogen were determined by gas chromatography using 5A molecular sieve column. In parallel the presence of nitrous oxide was monitored by FTIR spectrometer.

RESULTS AND DISCUSSION

1. Catalyst Preparation

The challenge in the preparation of perovskites, or of other multicomponent phases for applications as highly active catalysts at relatively low temperatures is to assure not only the complete formation of the required phase, but also a large, highly defective surface of the material. This necessarily requires methods allowing the formation of the new phase at low temperatures, which usually call for solution of all components as the starting precursor. Such solution based methods, although efficient, may be long and costly.

Our suspension based method reduces the overall preparation time, eliminates the use of complexing and/or precipitating agents, and reduces the volume of by-product gases, apparently without compromising the quality of the final product. By this method relatively high specific surface area (Table 1), nearly phase pure perovskite powders were obtained for all compositions except for that of LFCu, for which a mixture of $LaCuO_4$, CuO and $LaFeO_3$ was obtained. Evidently, at this nominal composition a single perovskite phase is not stable. Nevertheless, for comparison this mixed catalyst was included in the study of the catalytic activity. Fig. 1 gives an example of X-ray diffraction patterns for three perovskite compositions (LSCuF, LSNC and LSCuA). As indicated by the position of the principal peaks, the size of the crystal unit decreases from 0.3897 nm for LSCuF to 0.3805 nm for LSCuA, reflecting the difference between the ionic radius of Fe^{3+} and Al^{3+}. Although this factor has rarely been discussed in relation with the activity of a given composition, it may have an important effect.

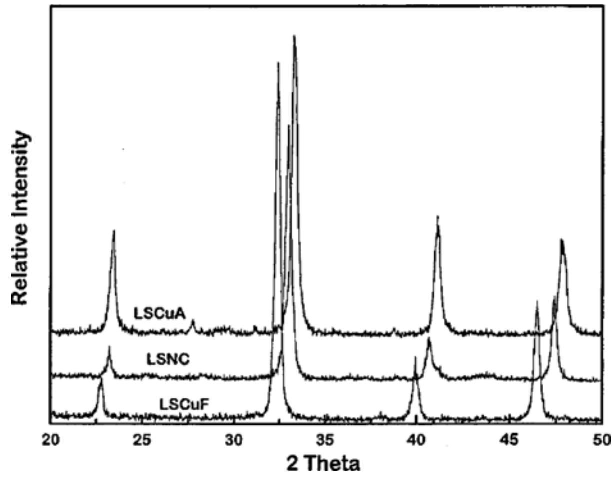

Fig. 1. XRD patterns for three selected perovskite compositions.

2. Catalytic Activity in Nitric Oxide Decomposition

Initial exploratory experiments to determine the apparent activities in the absence of oxygen in the feed and to identify the potentially best performing catalyst were mostly run with a single reactor charge, but at several flowrates, partial pressures of nitric oxide and temperatures between 723 to 923 K. The experimental conversion data as a function of temperature for the case of 50 mL/min total flowrate and 5 vol% (0.05 bar) nitric oxide are presented in Fig. 2. For other conditions (flowrates and partial pressure) only selected conversion data, at 773 K and 923 K respectively, are presented in Table 2 for several catalysts. Table 3 presents separately the data for LSNCF catalyst, for which the performance was evaluated at a wider range of experimental conditions. In all cases the experiments were carried out over several days, overnight the catalyst being left to cool to ambient temperature under a flow of pure helium. Over the period of tests lasting at least 30 h no diminution of activity of any of the catalyst was observed. Thus, similarly as was found previously in the case of combustion [Klvana et al., 1997], good stability and durability seems to be the attractive characteristics of these perovskite cat-

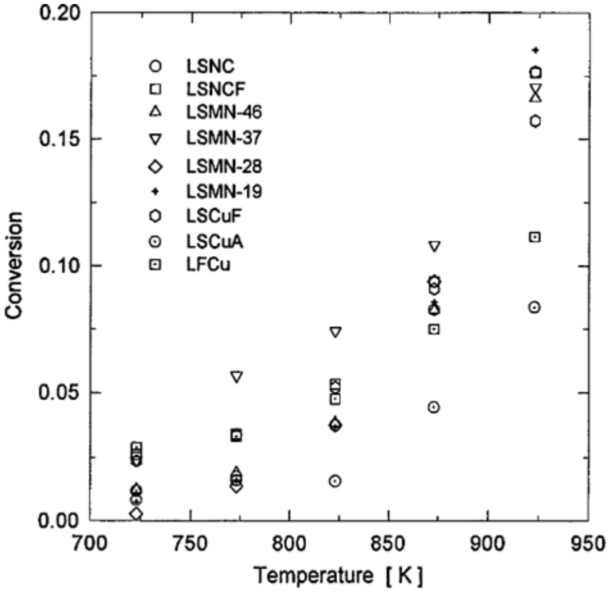

Fig. 2. Conversions of nitric oxide to nitrogen over several perovskite catalysts versus temperature; 1 g catalyst, 50 mL/min total flowrate, 5 vol% nitric oxide in helium.

Table 2. Selected activity data for new perovskite catalysts

Catalyst	Flowrate mL/min	P^i_{NO} bar	W/F $g \cdot s/\mu mol$	x_{773K} %	x_{923K} %	k_{773K} $\mu mol/g \cdot s \cdot bar$	k_{923K} $\mu mol/g \cdot s \cdot bar$
LSNC	100	0.05	0.27	0.9	12.3	0.7	10.0
LSNCF	100	0.05	0.25	0.7	10.4	0.6	9.1
LSMN-46	100	0.05	0.27	0.9	11.7	0.7	9.4
LSMN-37	100	0.05	0.26	1.4	8.0	1.0	6.5
LSMN-28	100	0.05	0.27	0.8	14.3	0.6	11.4
LSMN-19	100	0.05	0.27	1.0	12.7	0.8	10.3
LSCuF	100	0.05	0.27	1.9	10.9	1.4	8.6
LSCuA	100	0.05	0.26	0.7	5.0	0.5	4.0
LFCu	100	0.05	0.27	0.9	5.9	0.7	4.6
LSNC	75	0.02	0.92	2.0	12.6	1.1	7.4
LSMN-46	75	0.02	0.92	1.7	14.4	0.9	8.6
LSMN-28	75	0.02	0.93	1.1	17.0	0.6	10.1
LSMN-19	75	0.02	0.92	0.8	14.5	0.4	8.7
LSCuF	75	0.02	0.93	3.6	13.6	1.9	7.9
LSCuA	75	0.02	0.90	1.4	6.5	0.8	3.8
LSNC	15	0.02	4.84	13.1	38.6	1.4	5.1
LSMN-46	15	0.02	4.84	15.6	44.8	1.7	6.2
LSMN-28	15	0.02	4.87	5.4	38.9	0.6	5.1
LSMN-19	15	0.02	4.83	8.7	35.3	0.9	4.5
LSCuF	15	0.02	4.83	24.2	45.8	2.9	6.4
LSCuA	15	0.02	4.80	17.2	27.8	2.0	3.4

alysts. Over none of the catalysts formation of nitrous oxide as an intermediate product was observed.

Conversion data in Table 2 and in Fig. 2 reveal some important characteristics of the new perovskites. First, as compared to activities of previously studied compositions [Yasuda et al., 1990; Teraoka et al., 1990; Shimada et al., 1988] most of the new compositions are significantly more active, even though the specific surface areas are comparable, i.e. 10±2 m^2/g. For example for flowrates of 15 mL/min of 1 % nitric oxide over 1 g catalyst at 973 K the published conversions [Teraoka et al., 1993] varied between 3 to 47 %. The two highest reported conversions (47 and 45 %) were obtained for $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$ and $La_{0.8}Sr_{0.2}CoO_3$ respectively, whereas the lowest conversions were observed over manganites and oxygen saturated compositions such as $LaCoO_3$. In comparison, for such low flowrates, and the same quantity of catalyst but higher nitric oxide concentration in helium, we have observed at 923 K, 50 degrees lower, conversions between 28 and 46 %. Obviously, although SSA is an important factor, it is not the dominant characteristics of a highly active catalyst. This is illustrated even better by the data for LSCuF and LSCuA compositions of this study. These two copper containing compositions have similar formula differing only in the character of the central B-site cation. Although LSCuA has twice as high SSA as LSCuF and other compositions, its activity is at most temperatures the lowest. It is this central cation which seems to confer the prevailing character to the material. It may be speculated that this is in part due to a low electron conductivity expected in LSCuA. On the other hand, a poor activity of LFCu with respect to LSCuF may be attributed to the expected lower oxygen mobility in LFCu, which in fact was not a single perovskite phase, but rather a mixture of La_2CuO_4, $LaFeO_3$ and CuO. A single perovskite phase having a composition corresponding to this mixture, i.e. $LaFe_{0.34}Cu_{0.66}O_{3-\delta}$ can not apparently be formed at the employed preparatory conditions. Except for LFCu and LSCuA, relatively small difference in activities of the studied compositions is observed. Yet, some subtle differences such as the effect of partial pressure of nitric oxide and perhaps of oxygen, as well as different corresponding temperature effects on the activity are suggested by the conversion data. These become more evident through a kinetic analysis.

In view of an integral mode of the reactor operation, it is convenient to use a pseudo-first order model as the starting point. This allows the determination of apparent rate constants and their analysis with respect to experimental conditions. From the experimental conversions the corresponding rate constants were obtained. Values at 773 K and 923 K (k_{773} and k_{923}) were selected as representative and are entered in Tables 2, and 3. Should the first order model apply over all experimental conditions, for a given composition these values would be invariant with respect to contact time and partial pressure of nitric oxide. Inspection of data in Table 2, and particularly of those for LSNCF catalyst in Table 3 clearly shows that this is not strictly the case, even if taking into account experimental error. For example, at 923 K and 5 % nitric oxide the k_{923} (and consequently the corresponding rate) increases as the flowrate decreases. Furthermore, for a given contact time, the k_{923} significantly increases, as the partial pressure of nitric oxide

Table 3. Activity data for LSNCF at different experimental conditions

Flowrate mL/min	P^{i}_{ND} bar	W/F g · s/μmol	W g	x_{773K} %	x_{923K} %	k_{773K} μmol/g · s · bar	k_{923K} μmol/g · s · bar
50	0.050	0.54	1.0	3.39	17.62	1.3	7.3
75	0.050	0.34	1.0	2.11	13.23	1.2	8.5
100	0.050	0.25	1.0	0.73	10.36	0.6	9.1
10	0.100	2.10	1.5	-	76.43	-	6.6
20	0.100	1.04	1.5	16.28	43.52	1.6	5.3
50	0.100	0.40	1.5	4.94	23.67	1.2	6.5
50	0.050	0.85	1.5	10.19	26.52	2.5	7.3
100	0.050	0.41	1.5	3.39	16.32	1.7	8.8
100	0.025	0.82	1.5	6.59	21.26	3.3	11.9
200	0.012	0.77	1.5	3.44	14.29	3.6	16.5

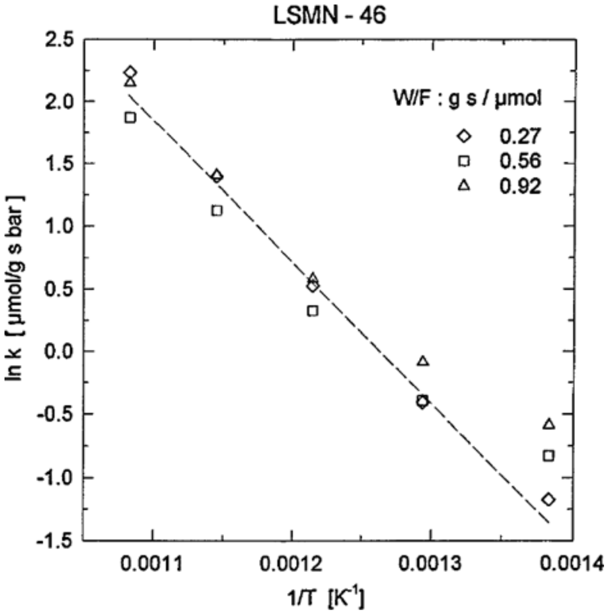

Fig. 3. Arrhenius plot for an integrated pseudo-first order model for the LSMN-46 catalyst; 1 g catalyst, three different contact times.

Table 4. Apparent kinetic parameters of the pseudo-first order rate model for nitric oxide decomposition over several new perovskite catalysts

Composition	E_{app} kJ/mol	ln k_o µmol/g · s · bar
$La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_{3-\delta}$	92	14.0
$La_{0.66}Sr_{0.31}Ni_{0.29}Co_{0.69}Fe_{0.02}O_{3-\delta}$	98	14.5
$La_{0.4}Sr_{0.6}Mn_{0.4}Ni_{0.6}O_{3-\delta}$	94	14.3
$La_{0.7}Sr_{0.3}Mn_{0.3}Ni_{0.7}O_{3-\delta}$	57	9.2
$La_{0.87}Sr_{0.13}Mn_{0.2}Ni_{0.8}O_{3-\delta}$	114	17.1
$La_{0.95}Sr_{0.05}Mn_{0.17}Ni_{0.83}O_{3-\delta}$	107	16.1
$La_{0.8}Sr_{0.2}Cu_{0.15}Fe_{0.85}O_{3-\delta}$	64	10.4
$La_{0.8}Sr_{0.2}Cu_{0.15}Al_{0.85}O_{3-\delta}$	70	10.3
$La_2CuO_3/CuO/LaFeO_3$	64	9.8

decreases. These effects, which seem to apply in a different way at lower temperatures (<~820 K) suggest a slow oxygen (product) desorption, and an inhibition by nitric oxide. Their changing influence on the reaction as the temperature changes correlates well with the changes due to temperature in the mechanism of methane combustion [Klvana et al., 1997]. In spite of these effects, for a given experimental condition, the data for higher temperatures may be fitted satisfactorily by a first order model, as shown in Figs. 3 and 4. Neglecting the discussed effects, the apparent activation energies for the tested samples were obtained and are presented in Table 4. These values which seem to be in agreement with the published data for other catalysts vary from as low as 57 kJ/mol for LSMN-37 to 114 kJ/mol for LSMN-28.

Although the activities of these new perovskite compositions in the decomposition of nitric oxide are at 773 K still about three orders of magnitude lower than required for practical use, the significant increase in the activity with respect to other perovskites, platinum or thermally stable transition metal oxides is encouraging. In view of a relatively high thermal stability as well

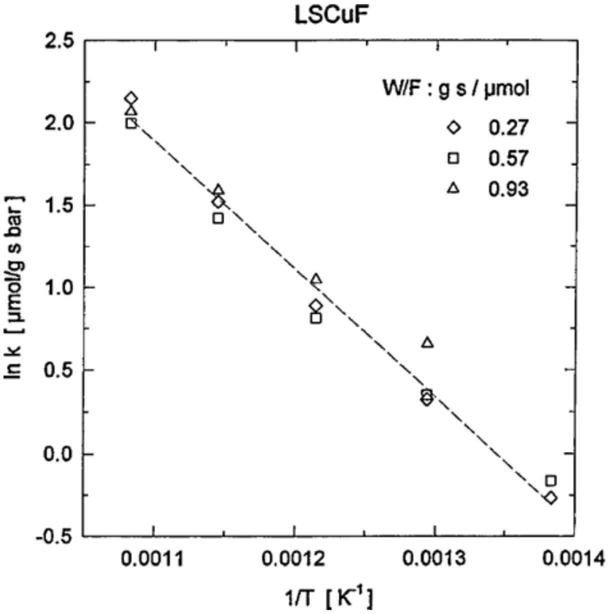

Fig. 4. Arrhenius plot for an integrated pseudo-first order model for the LSCuF catalyst; 1 g catalyst, three different contact times.

as a potentially reasonable resistance to poisoning by sulfur dioxide of these perovskites, further research is warranted.

CONCLUSIONS

While a significant progress in the quest for the development of a practical industrially applicable nitric oxide decomposition catalyst has been made over the last fifteen years, improving thereby the prospects of ever reaching this long sought goal, much remains to be done.

In terms of activities, at temperatures below 800 K, copper exchanged zeolites are at present the only system approaching the practical requirements.

In terms of thermal stability, and possibly resistance to poisoning, properly formulated perovskites seem to hold some promise as practical catalysts in spite of their still very low, as compared to zeolites, activities.

For example, as shown is this work, nickel, cobalt and/or copper based oxygen deficient perovskites with relatively high specific surface areas and with substantially improved activities, as compared to previously studied perovskites, may be designed. Several of these new perovskites exhibit at 923 K higher activities than those of previously reported best performing at 973 K. Although at 773 K the activities of the new perovskites are still up to three orders lower than those of the best zeolites, at 923 K, the difference is much smaller.

In view of their general versatility and their potential to serve as a model system to help the elucidation of the catalytic decomposition perovskites as a group merit further studies.

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