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Novel oxygen storage components for advanced catalysts for emission control in natural gas fueled vehicles

Yun-feng Chang, Jon G. McCarty

SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025, USA

Abstract

Advanced catalysts based on a novel oxygen storage component (OSC) were developed for emission control in natural gas fueled vehicles. The catalysts contain a manganese oxide (MnO_x) as the OSC supported on an inert $LaAlO_3$ perovskite and a noble metal component (Pd) supported on a separate high surface area refractory material, for example lanthana stabilized Al_2O_3. The MnO_x has higher oxygen storage capacity, and faster oxygen absorption and oxide reduction rates than the present commercial ceria-stabilized alumina support materials. Temperature programmed techniques and dynamic cycled experiments were used to measure oxygen storage capacity, activity for NO reduction and CO and CH_4 oxidation rates. Durability tests on a physical mixture of Pd-Mn/$LaAlO_3$ and Pt/Al_2O_3(La) demonstrated that a temperature excursion to 950°C for 30 min did not cause significant loss in catalyst activity for either NO reduction or CO or CH_4 oxidation. We have also shown that the MnO_x can be added to conventional three-way catalysts (TWC) to enhance their performance for NO_x reduction and CO or hydrocarbon oxidation.

Keywords: High temperature three-way catalyst (TWC); Oxygen storage component (OSC); Emission control for natural gas fueled vehicles; Manganese oxide (MnO_x)

1. Introduction

Natural gas has received increased attention as an alternative fuel for motor vehicles because of its potential technical, economic, and environmental advantages. Natural gas vehicles (NGV) generate exhaust gas with extremely low photochemical reactivity [1], produce low cold-start CO emission [2], and have zero evaporative emission. On the other hand, NO_x emissions as well as CO and unburned CH_4 (a much more powerful greenhouse gas than CO_2 [3,4]) in NGV exhaust need to be greatly reduced. Conventional three-way catalysts (TWC) currently used for gasoline-vehicle exhaust emission control showed poor methane conversion for NGV exhaust gas [5]. Therefore, new catalyst formulations are needed to reduce levels of these pollutants in NGV exhaust to meet ultra-low emission vehicle (ULEV) standard.

Conventional TWC presently used in automobile catalytic converters work well for reducing CO, hydrocarbons (HCs), and NO_x emissions in strict stoichiometric combustion exhaust. However, most pollution (80%) is produced under conditions outside the stoichiometric window. Therefore, to meet the new stringent emission standards, particularly, the ULEV standards, catalysts which function in a wider air-to-fuel ratio range must be developed. They must be able to supply oxygen to oxidize CO and HCs when exhaust is fuel rich and remove

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excess oxygen when it is lean. The key to such catalysts is to find an OSC which has superior performance than Ce-based OSC [6,7]

The objectives of this work was to develop oxygen storage materials with higher capacity, faster oxygen absorption and oxide reduction rates than present commercial ceria supported on alumina, to find supports which have high surface area and highly sintering resistant, and to formulate catalysts to be used for high-temperature three-way emission control for natural gas fueled vehicles.

In this work, we report MnO_x as an OSC supported on a variety of highly refractory materials that can be used for NO_x, CH_4, and CO reduction in NGV exhaust gas. Both temperature programmed and dynamic cycled techniques were developed and used to measure the oxygen storage capacity and catalytic activity for NO_x, CH_4, and CO reduction under dynamic cycled conditions similar to that from an engine manifold.

2. Experimental

2.1. Materials

Catalyst supports, $LaAlO_3$ perovskite, $LaAl_{11}O_{18}$ (hexaaluminate), and $BaAl_{12}O_{19}$ (hexaaluminate) were prepared using a sol–gel technique and supercritical drying [8] while lanthanum stabilized Al_2O_3(La), and $BaAl_2O_4$ spinel were prepared by ball milling and impregnation procedures. 10%Ce/Al_2O_3 was prepared by impregnation. The final calciantion temperature was 1250°C for $LaAl_{11}O_{18}$, 1025°C for $LaAlO_3$, 1000°C for $BaAl_{12}O_{19}$ and 10%Ce/Al_2O_3, 1100°C for Al_2O_3(La), and 800°C for $BaAl_2O_4$.

2.2. Temperature programmed experiments

Temperature programmed oxidation (TPO) in diluted oxygen, reduction (TPRd) in diluted hydrogen, and reaction (TPR) experiments were carried out in a microreactor. An amount of 0.1 g of catalyst powder was used. Reaction effluents were analyzed by an on-line quadrupole mass spectrometer (EAI).

2.3. Dynamic cycled experiments

Fast (~2 Hz) and slow (0.25 Hz) dynamic cycled experiments were conducted in a dynamic switched flow micro-reactor system illustrated in Fig. 1. The amount of catalyst used was 50 mg in powder form. With balanced resistance to flow (pressure drop across the microreactor bed and a by-pass metering valve) dilute oxygen and pure helium are alternately switched into net reducing mixtures for slow and fast transients.

3. Results and discussion

Fig. 2 gives the X-ray diffraction pattern of 8%Mn supported on $LaAlO_3$ perovskite. The XRD characteristics are exactly the same as $LaAlO_3$ alone, indicating that the support is exclusively perovskite phase and after impregnation with Mn salt solution and calcination at 800°C does not change the support. This is also supported by BET surface area measurements

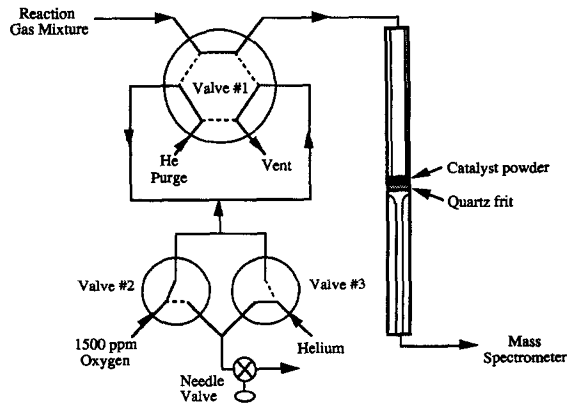

Fig. 1. Schematic diagram of the dynamic switched flow reactor apparatus used for cycling experiments. The needle valve is used to balance pressures to minimize flow bursts and the 6-port valve is used to by-pass the switched-in flow.

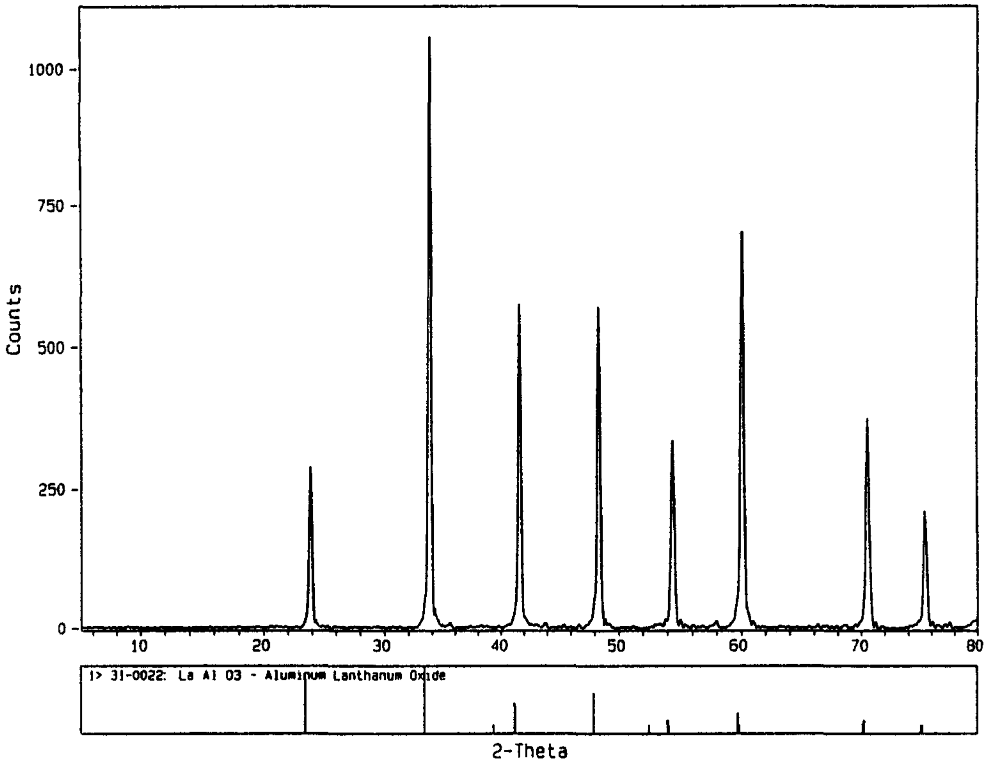

Fig. 2. XRD patterns of $LaAlO_3$ perovskite loaded with 8 wt% Mn powder sample.

($LaAlO_3$: 16.2 m^2/g vs. 8%Mn/$LaAlO_3$: 14.7 m^2/g) that no significant surface area changes occurred after impregnation.

Table 1 presents the oxygen storage capacity of MnO_x supported on a variety of supports, measured by TPO and TPRd using hydrogen. These results clearly show that Mn/$LaAlO_3$ catalysts have large OSC. Fig. 3, a typical TPO profile of supported reduced MnO_x on $LaAlO_3$ perovskite, shows that MnO_x has good O_2 uptake (oxidation) and O_2 release (reduction) rates at temperatures below 600°C. This performance was confirmed by TPRd and was significantly better than that of ceria-stabilized alumina.

Irreversible formation of complex oxides (aluminates) may be the major reason for industry's past failure to develop stable emission control catalysts using first-row transition metal oxides (Mn, Fe, Co, Ni, Cu). These single metal oxides sinter rapidly when unsupported and irre-

Table 1
Temperature programmed measurements of total OSC of supported MnO_x

Catalyst	OSC by TPO (μmol O_2/g_{cat})	OSC by TPRd (μmol H_2/g_{cat})	Theoretical [a] (μmol O/g_{cat})
2 wt% Mn/$LaAlO_3$	94	225	182
4 wt% Mn/$LaAlO_3$	114	290	364
8 wt% Mn/$LaAlO_3$	225	555	728
4 wt% Mn/Al_2O_3 (La)	81	285	364
4 wt% Mn/$BaAl_{12}O_{19}$	66	203	364
4 wt% Mn/silicalite	34	272	364

[a] $Mn_2O_3 \rightarrow 2MnO + 1/2O_2$.

versibly react with common alumina-based supporting oxides at moderate temperatures to form inactive aluminate spinels [9,10]. Thermochemical analysis suggests that the combination of a stable alkaline earth (e.g. Ba) or rare earth (e.g. La) oxide with alumina will yield complex oxides of sufficient stability that they cannot form aluminate oxides. We believe that no transition metal other than manganese can remain in the +2 valence state and resist reduction to the readily sintered, and difficult to re-oxidize, metallic form under rich A/F conditions nor remain in the +3 valence state under lean conditions found in a four cycle engine exhaust. High capacity for oxygen and rapid oxidation and reduction rates are possible with such a moderate valence swing.

Fig. 4 gives the typical on-line waveforms for slow and fast switch experiments conducted on a powder catalyst sample (Pd-Mn/$LaAlO_3$) in the absence of reactions. An argon trace was used to locate the switch front as the gas mixture arrives at the downstream analyzer. Key properties determined by these experiments are the rates of reduction and reoxidation, the extent of specific oxidation and reduction of the oxide, and the mean oxygen level as functions of temperature, average stoichiometry, and amplitude of the swing in O_2 partial pressure.

Due to its simplicity and its importance in emission control using TWC catalysts, the oxidation of CO by O_2 was chosen to measure the dynamic oxygen storage capacity. During the cycled experiments, the concentration CO was kept constant (0.3 vol%) while that of O_2 was alternated between 0.05 vol% and 0.20 vol%. This was achieved by having constant 0.05 vol% O_2 added to the system and adding 0.15 vol% O_2 from the switched-in flow. In effect, in the CO-rich half-cycle, it has net excess 0.2 vol% CO and in the O_2-rich half-cycle a net excess 0.05 vol% O_2. Therefore, if the catalyst does not show any oxygen storage capacity, in the O_2-rich half-cycle, the level of O_2 breakthrough will be higher than 0.05 vol%. Levels of O_2 breakthrough depend on the activity of catalysts.

3.1. 1%Pd-10%Ce/Al_2O_3

Fig. 5a gives the results of ceria (10 wt% Ce) stabilized γ-Al_2O_3 supported 1 wt% Pd for the oxidation of CO. Complete conversion of CO was achieved in the O_2-rich half-cycle at $\geq$

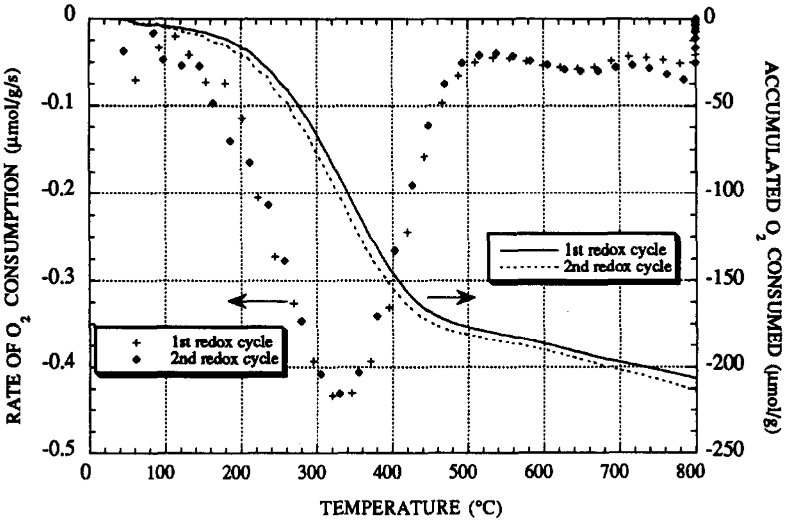

Fig. 3. TPO profile of the $LaAlO_3$ perovskite supported reduced MnO_x (8 wt% Mn) catalyst by 1 vol% O_2 in He; flow rate: 40 cm^3/min; catalyst mass: 0.1 g; heating rate: 30°C/min.

350°C. This catalyst is much more active than the supported MnO_x catalysts. At temperatures above 350°C, levels of O_2 breakthrough decrease with increase of temperature. The levels of O_2 breakthrough at ≥ 350°C are below 0.05 vol%. However, no complete removal of O_2 was achieved. The level of O_2 breakthrough at high temperatures is significantly higher than $LaAlO_3$ or La_2O_3 stabilized γ-Al_2O_3 supported MnO_x at the corresponding temperatures, suggesting that this catalyst has lower OSC than 8 wt%-Mn/$LaAlO_3$ and 8 wt%-Mn/Al_2O_3(La). The low oxygen storage capacity of 1%Pd-10%Ce/Al_2O_3 is due to ceria not because of the γ-Al_2O_3 support since 1 wt% Pd and 10 wt% Ce supported on $LaAlO_3$ also has poor oxygen storage performance (see Fig. 6a). Potential negative effect caused by presence of Pd can also be ruled out as $LaAlO_3$ supported 1 wt% Pd and 8 wt% Mn shows as good oxygen storage performance as $LaAlO_3$ supported MnO_x alone.

TPO and TPR measurement results (not given) show that MnO_x has superior oxygen storage performance than ceria. Though the use of MnO_x is critically important for achieving good oxygen storage performance, supports also play very important roles. Among the supports we investigated, $LaAlO_3$ and La_2O_3-stabilized Al_2O_3 are the best.

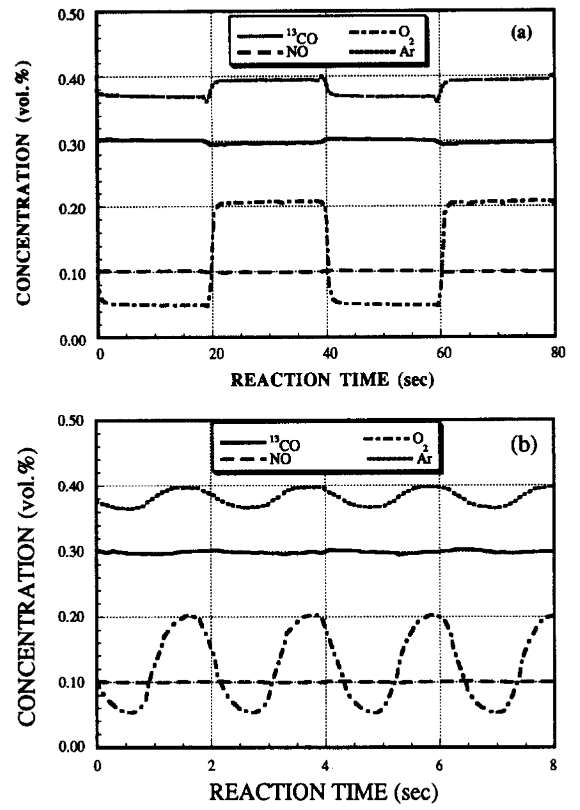

Fig. 4. Typical on-line gas mass spectrometric analysis for the dynamic switched flow reactor showing composition waveform in the absence of reaction. 20 mg of 1 wt% Pd and 8 wt% Mn supported on $LaAlO_3$; reactant gas composition, 0.3 vol% CO, 0.05 (reducing) and 0.2 (oxidizing) vol% O_2 with 0.36 vol% (reducing) and 0.40 vol% (oxidizing) Ar tracer in He; total flow, 100 cm^3(NTP)/min; (a) half cycle time, 20 s; (b) half cycle time, 1 s; GHSV: 600000 h^{-1}.

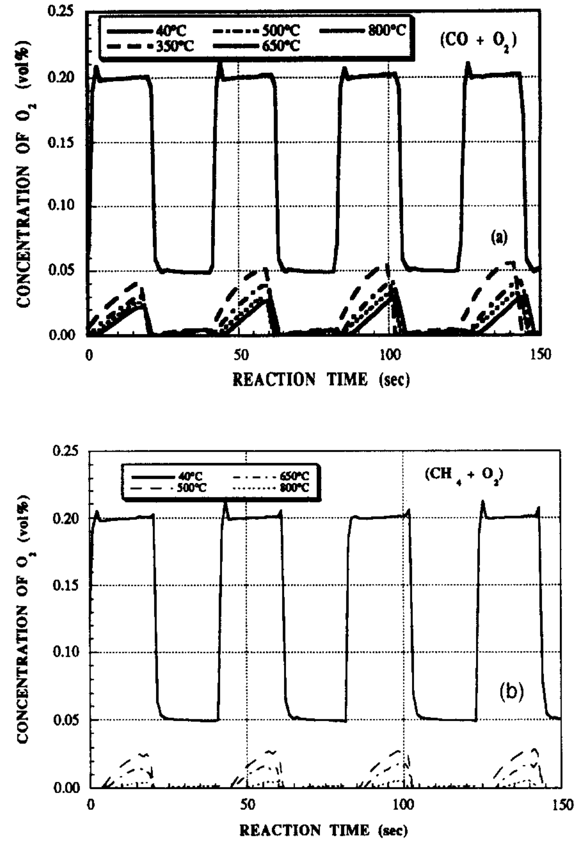

Fig. 5. Dynamic slow cycle redox reactions of CO and CH_4 with O_2 over the 10 wt%Ce-stabilized γ-Al_2O_3 supported 1 wt% Pd catalyst. Half cycle time, 20 s; reactant gas composition, (a) 0.3 vol% CO, 0.05 (reducing) and 0.2 (oxidizing) vol% O_2 with Ar tracer in He; (b) 0.05 vol% CH_4, 0.05 (reducing) and 0.2 (oxidizing) vol% O_2 with Ar tracer in He; total flow, 100 cm^3(NTP)/min; catalyst mass, 0.02 g; GHSV: 600000 h^{-1}.

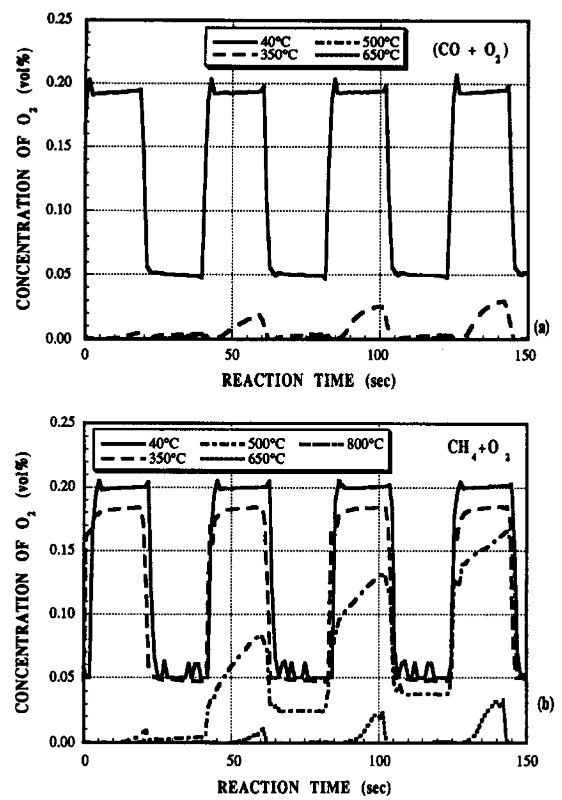

Fig. 6. Dynamic slow cycle redox reactions of CO and CH_4 with O_2 over the $LaAlO_3$ supported 1 wt%Pd and 8 wt%Mn catalyst. Half cycle time, 20 s; reactant gas composition, (a) 0.3 vol% CO, 0.05 (reducing) and 0.2 (oxidizing) vol% O_2 with Ar tracer in He; (b) 0.05 vol% CH_4, 0.05 (reducing) and 0.2 (oxidizing) vol% O_2 with Ar tracer in He; total flow, 100 cm^3(NTP)/min; catalyst mass, 20 mg; GHSV: 600000 h^{-1}.

The dynamic switched oxidation of CH_4 by O_2 over 1 wt%Pd-10 wt%Ce/Al_2O_3 and 1 wt%Pd-8%Mn/$LaAlO_3$ are given in Fig. 5b and Fig. 6b, respectively. Though, in terms of oxygen storage performance, 1 wt%Pd-10 wt%Ce/Al_2O_3 is inferior to 1 wt%Pd-8%Mn/$LaAlO_3$ the catalytic activity of the former (not shown) is higher than the latter for oxidation of CH_4. This difference cannot be the result of interaction between Pd and Ce because 1 wt%Pd-10 wt%Ce/$LaAlO_3$ has similar activity as 1 wt%Pd-8%Mn/$LaAlO_3$. Thus, the high activity of ceria stabilized γ-Al_2O_3 supported Pd is the result of high dispersion of Pd on Al_2O_3 which has a BET surface area of $140 m^2/g$ compared to 16 m^2/g for $LaAlO_3$.

For this reason, we may prefer to have the catalytically active noble metal component supported on high surface area supports, for instance, $LaAl_{11}O_{18}$ or La_2O_3-stabilized Al_2O_3. The high activity for CH_4 oxidation and reforming to form NO_x-reducing CO and H_2 shown by 1 wt%Pd-10 wt%Ce/Al_2O_3 suggests the use of Pd-based catalyst can substantially reduce NO_x and CH_4 emission in natural gas vehicles.

3.2. *Physical mixtures of Mn/$LaAlO_3$ and Pd/$LaAl_{11}O_{18}$ or Pt/CeO_2/Al_2O_3*

We have demonstrated that it is not necessary to support both the OSC component (MnO_x) and noble metal on the same perovskite support. In fact, it is preferable to support the precious metal on a separate, stable, high surface area support, e.g. $LaAl_{11}O_{18}$, so that high dispersion of the metal component can be achieved. Based on this idea, we conducted dynamic cycle experiments with both (NO, ^{13}CO, and O_2) and (NO, CH_4, and O_2) simulated exhaust gas streams with a physical mixture of 10 mg 1 wt%Pt-8 wt%Mn/$LaAlO_3$ and 10 mg 1 wt%Pt-10 wt%Ce/Al_2O_3, and with a physical mixture of 10 mg 1 wt%Pt-8 wt%Mn/$LaAlO_3$ and 10 mg 2wt%Pd/$LaAl_{11}O_{18}$. Previously, we found that calcination of $LaAl_{11}O_{18}$ hexaaluminate supports at 1150°C for 72 h can ensure that these supports remained stable during methane combustion after repeated ($\approx$ 100) excursions to 950°C [11]. We have also examined the methane conversion activity of 1 and 2 wt% Pd and Pt catalysts supported on $LaAl_{11}O_{18}$ using temperature programmed techniques [11].

Results in Fig. 7(a) and Fig. 7(b) show that for NO reduction by CO, complete removal of O_2 and complete reduction of NO are achieved at temperatures above 300°C. This beneficial effect must be the result of the combination of the greater activity of 1 wt%Pt-10%Ce/Al_2O_3 with the greater oxygen storage capacity of the 1 wt%Pt-8 wt%Mn/$LaAlO_3$. For NO reduction by CH_4, complete removal of O_2 and complete NO conversion are achieved $\geq$ 500°C.

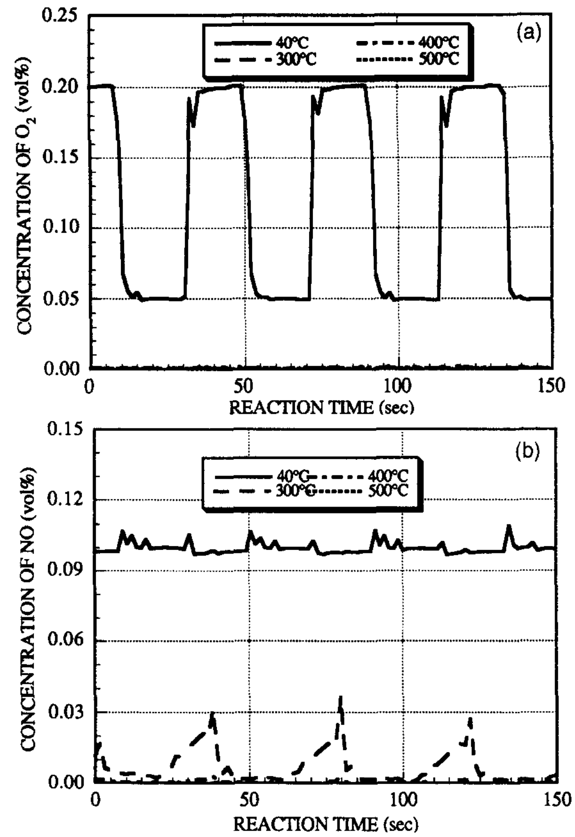

Fig. 7. Dynamic slow redox reaction of CO, NO, and O_2 over physically mixed ceria (10 wt% Ce) stabilized Al_2O_3 supported 1 wt% Pt and $LaAlO_3$ perovskite supported 1 wt% Pt and 8 wt% Mn catalyst at 40–800°C. Half cycle time, 20 s; reactant gas composition, 0.4 vol% ^{13}CO, 0.1 vol% NO, and 0.05 (reducing) and 0.2 (oxidizing) vol% O_2 with Ar tracer in He; total flow, 100 cm^3(NTP)/min; catalyst mass, 50 mg each; GHSV: 240000h^{-1}.

Similar beneficial effects are also observed for the physical mix of 1 wt%Pt-8 wt%Mn/$LaAlO_3$ and 2wt%Pd/$LaAl_{11}O_{18}$ for both NO reduction by CO and NO reduction by CH_4. Though addition of 2wt%Pd/$LaAl_{11}O_{18}$ led to improved CH_4 oxidation activity it is much less effective than 1 wt%Pt-10 wt%Ce/Al_2O_3 despite both have high surface area. The superior performance of 1 wt%Pt-10 wt%Ce/Al_2O_3 to 2 wt%Pd/$LaAl_{11}O_{18}$ for NO reduction by CH_4 may be due to higher surface area (141 vs. 95 m^2 g^{-1}) and deserves further investigation.

4. Durability of mixed three-way catalysts

Aging experiments were conducted on the physical mix of 1 wt%Pt-10 wt%Ce/Al_2O_3 and 2 wt%Pd/$LaAl_{11}O_{18}$ catalyst. This was done by heating repeatedly to 800°C and a single excursion to 950°C during reduction of NO by CO. We found that aging leads to some loss of oxygen storage capacity, and lower activity for NO reduction. However, the aged catalyst retains good activity for NO reduction and the conversion of NO is greater than 70% at ≥ 500°C (Table 2). The loss of NO reduction activity was caused by decreasing surface area (sintering) not by the formation of complex Mn oxides. This demonstrates that our catalyst formulations not only give excellent performance for CH_4 oxidation and NO reduction but also can sustain good performance following a high temperature excursion to 950°C.

The above results demonstrate that noble metals are essential components in TWCs for

Table 2

Comparison of performance of a physical mixture of 1 wt%Pt-8 wt%Mn/$LaAlO_3$ and 2 wt%Pd/$LaAl_{11}O_{18}$ for NO reduction by CO before and after ageing at 950°C for 30 min

Temperature (°C)	Fresh catalyst NO conversion (vol%) CO-rich cycle	O_2-rich cycle	OSC activity O_2 breakthrough	Catalyst aged at 950°C NO conversion (vol%) CO-rich cycle	O_2-rich cycle	OSC activity O_2 breakthrough
300	85	80	small	70	72	significant
400	98	90	small	85	80	significant
500	~ 100	82	very small	98	84	small
600	~ 100	80	very small	98	76	very small
700	~ 100	78	very small	98	74	very small

the reduction of NO_x (mostly NO). When using CNG fuel, it is also very essential that the TWC convert some methane into reducing gases H_2 and CO to insure complete reduction of NO. While the supported manganese oxides show some activity for methane conversion, especially above 500°C, their activity under reducing conditions is low relative to the noble metals. Therefore, to be effective for NO_x reduction using CNG fuels with lower CO and higher CH_4 levels in the engine exhaust gases, our manganese components for enhanced oxygen storage must be combined with a very active noble metal-based component. We anticipate either adding Pd or Pt to the $MnO_x/LaAlO_3$ or adding supported noble metals as a separate phase for both NO reduction and the production of reducing gas.

5. Conclusions

MnO_x supported on $LaAlO_3$ perovskite is superior to ceria in several ways: (i) it directly and rapidly absorbs oxygen without need for noble metals to promote the rate of oxygen absorption; (ii) it exhibits a larger capacity for oxygen storage over a wide temperature range; (iii) it directly oxidizes CH_4; and (iv) with assistance of noble metals, it shows steam reforming or partial oxidation activity (converting CH_4 and steam into CO and H_2). This ability to generate CO and H_2 under oxidizing conditions is especially important for reducing NO_x emissions in NGV exhaust gas.

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