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Steady-state isotopic transient kinetic analysis on Pd-supported hexaaluminates used for methane combustion in the presence and absence of NO

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Abstract

This paper presents a study for the combustion of methane in the presence and absence of NO over hexaaluminates ($La_{1-X}Sr_XMnAl_{11}O_{19}$) and Pd-supported hexaaluminates ($Pd/La_{1-X}Sr_XMnAl_{11}O_{19}$). All the catalysts were subjected to a reaction cycle comprising of (1) CH_4+O_2, (2) CH_4+O_2+NO, and (3) CH_4+O_2 reactions at temperatures between 300 and 700°C. Steady-state isotopic transient kinetic analysis (SSITKA) technique was employed to determine the surface lifetimes (τ), average site activities (k), and surface concentrations (N) of each relevant species during the reactions (1) and (2), as described above, on $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ and 0.9% $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$. The SSITKA experiments were performed at temperatures of 360–440°C.

Steady-state results showed that the contribution of homogeneous gas phase reactions are appreciable in the presence of NO at temperatures above 650°C. Steady-state and SSITKA reactions on $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ suggested that methane and NO oxidation occur on the catalyst surface at 440°C. Steady-state and SSITKA reactions on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ showed that the presence of NO_2 (formed via NO and O_2) boosted the site activity required for the formation of CO_2. In the reaction where NO is involved, NO acts indirectly as chain initiator in the form of NO_2, and also as chain terminator.

Keywords: Steady-state isotopic transient kinetic analysis; Hexaaluminates; Surface lifetimes; Average site activities; Surface concentrations

1. Introduction

Catalytic combustion offers a alternative means to thermal combustion of methane in stationary sources, because combustion is catalytically stabilized under fuel lean conditions, thus suppressing emissions of pollutants such as nitrogen oxides. For practical applications, thermally stable catalyst materials need to be developed because of the high operation temperatures (>1200°C) required. It has been reported by several researchers [1–8] that catalytic materials based on hexaaluminate compounds show good thermal stability and can maintain a large surface above 1300°C. However, this type of materials exhibits relatively low activity compared to other oxides such as perovskites resulting in higher light-off temperatures for the combustion of methane [9]. In general, a good catalyst should be able to initiate the surface reaction at low temperatures (<500°C, [10]). Oxide

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type catalysts have gained importance over noble metal catalysts due to their high temperature stability, however, their lower combustion activity compared to noble metals is a serious drawback. Among the noble metals, Pd is known to have the highest activity for the combustion of methane as well as the lowest volatility. Sekizawa et al. [11] reported that supporting Pd on hexaaluminates led to a higher activity for the combustion of methane compared to undoped hexaaluminates. Furthermore, they showed that Pd supported on manganese-containing hexaaluminates (Pd/$La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$) did not exhibit a decrease in the methane activity at high temperatures. Such a decrease is typically observed with Pd-supported oxides due to the decomposition of PdO to Pd. The loss of activity at temperatures above 700°C was linked to the lower methane combustion activity of metallic Pd compared to PdO_x [10–14].

This paper presents a study for the combustion of methane in the presence and absence of NO over hexaaluminates and Pd-supported hexaaluminates. Steady-state isotopic transient kinetic analysis (SSITKA), as well as the conventional steady-state reaction techniques, were employed to examine these reactions.

2. Experimental

2.1. Catalysts

The preparation of catalysts has been described in detail elsewhere [15,16]. The different types of catalysts used in this study are compiled in Table 1. Briefly, the catalysts were prepared from an aqueous solution containing appropriate amounts of the nitrate salts of metals. The corresponding hydroxides were precipitated by adding ammonium carbonate ($La_{1-X}Sr_XMnAl_{11}O_{19}$, X=0, 0.4, 0.8), or ammonium hydroxide ($La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$) to the solution. The solution was then filtered and the precipitate was washed with distilled water. The resulting material was dried at 120°C for 12 h. The catalysts were calcined at 1200°C for 2 h or 1400°C for 5 h. A series of hexaaluminates, $La_{1-X}Sr_XMnAl_{11}O_{19}$ (X=0.0, 0.4) was loaded with Pd (0.9 wt.%), using aqueous impregnation of catalysts with $PdNO_3$. All catalysts had been calcined at 1400°C prior to Pd impregnation. The Pd-loaded catalysts were dried and calcined at 1200°C for 2 h.

The surface areas of the catalysts were measured by N_2 physisorption at −196°C using the BET relation. The phase composition of the catalysts was determined by powder X-ray diffraction (XRD) using a Philips X'pert System X-ray diffractometer with monochromatized Cu Kα radiation. The XRD instrument was operated at 40 kV and 30 mA. The spectra were scanned between 10 and 80° (2Θ) at a rate of 2.4°C min^{-1}. Inductive coupled plasma (ICP) analysis was used to determine the Pd loading on hexaaluminates.

2.2. Steady-state reactions

Methane oxidation was carried out in the presence and absence of NO on the catalysts listed in Table 1, and also in the gas phase without a catalyst. The standard reactions studied were the following:

$$CH_4+2O_2 \rightarrow CO_2+2H_2O \qquad (I)$$

$$CH_4+3O_2+2NO \rightarrow CO_2+2H_2O+2NO_2 \qquad (II)$$

Table 1
Compilation of the catalysts and reactions

Catalysts	BET surface area[a] (calcination temperature, °C)	Phases determined by XRD[a]	Reactions carried on
$LaMnAl_{11}O_{19}$	34 (1200)	Hexaaluminate	CH_4+O_2, CH_4+O_2+NO
$La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3)	50 (1200)	Hexaaluminate	CH_4+O_2, CH_4+O_2+NO
$La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (OH)	9 (1200)	Hexaaluminate+α-alumina	CH_4+O_2, CH_4+O_2+NO
$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$	12 (1400)	Hexaaluminate	CH_4+O_2, CH_4+O_2+NO, SSITKA
0.9% Pd imp. $LaMnAl_{11}O_{19}$	14 (1200)	Hexaaluminate	CH_4+O_2, CH_4+O_2+NO
0.9% Pd imp. $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$	14 (1200)	Hexaaluminate	CH_4+O_2, CH_4+O_2+NO, SSITKA

[a] Detailed explanation of BET surface areas and the XRD patterns of the catalysts were given in [16] as well.

A fixed-bed laboratory-scale reactor system (system 1) was used to check the steady-state activity of the catalysts for methane combustion. Details of the reactor system and reaction conditions are given elsewhere [16].

Steady-state experiments were also carried out in a smaller reactor (system 2), described in the transient studies section, with a total flow rate of 30–50 cc min^{-1} to determine the optimum conditions for the transient experiments. These studies were carried out at temperatures between 300 and 700°C with 20–150 mg catalyst loading. NO, CH_4, and O_2 concentrations were varied. For reaction studies, concentrations of 2.4% CH_4, 6% O_2 and 2.3% NO were used. Some of the catalysts were also kept on-stream for 72 h at 700°C for reactions (I) and (II) to check for possible deactivation. Arrhenius plots were obtained under differential conditions starting from low temperature to high temperature. All experiments were carried out two or three times starting with fresh catalyst to confirm the reproducibility of the data.

In addition, the $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ catalyst was tested for the reaction of CH_4+NO in the absence of oxygen with a total flow rate of 33 cc min^{-1}, reactant concentrations of 2.4% CH_4 and 2.3% NO, and at temperatures of 600 and 700°C. These reactions were also carried out in the gas phase without a catalyst to determine the contribution of possible homogenous gas phase reactions.

2.3. *Study-state isotopic transient kinetic analysis (SSITKA) studies*

SSITKA was used to determine the surface lifetimes (τ), average site activities (k=reciprocal of surface lifetime), and surface concentrations (N) of each relevant species during methane combustion with and without NO.

Transient experiments were performed in a microreactor consisting of a 4 mm ID straight quartz tube. A detailed description of the reaction system can be found in [17]. Ultra-high purity gases were used for the reactions. The labeled gases, $^{13}CH_4$ and 5% ^{15}NO in He were obtained from Isotec. The non-labeled gases, $^{12}CH_4$ with 5% Ar and 5% ^{14}NO with 5% Ne (He balanced) were obtained from Linde and Liquid Carbonics, respectively. In order to account for the gas phase hold-up, nonreactive inert tracers were used. For the isotopic switches of CH_4, Ar was used as an inert tracer, whereas Ne was used for the NO switches. Helium was used as diluent in all cases. CH_4 and NO transients were obtained during reactions (I) and (II) on the 2% Pd impregnated $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ and $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ catalysts. The transient experiments entailed a switch of the isotopic composition of the reactants ($^{12}CH_4$ to $^{13}CH_4$, or ^{14}NO to ^{15}NO) at steady state followed by continuously monitoring the gas phase concentration of reactants and products of interest in the reactor effluent using a quadrupole mass spectrometer (MS) interfaced with a microcomputer for data acquisition.

Achievement of steady state prior to isotopic switches was monitored by on-line gas chromatographic (GC) analysis of the reaction products using a Varian 3700 GC equipped with a thermal conductivity detector (TCD). The reactor effluent was separated isothermally using a Porapak-Q column. Subsequently, isotopic switches from $^{12}CH_4$ to $^{13}CH_4$ and back, and then from ^{14}NO to ^{15}NO (for reaction (II)) were performed at temperatures between 350 and 500°C with a total pressure of 1.6 atm.

In a separate study, pressure transient analysis (PTA) was performed on Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ and $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 360 and 440°C. These experiments entailed, first, the partial $^{18}O_2$ exchange of the catalysts. After passing 3% $^{18}O_2$ in helium for 2 min, the system was purged with helium for 5 min and subsequently NO/He, $^{15}NO+O_2$, and $CH_4+^{15}NO+O_2$ mixtures were passed through the partially ^{18}O-exchanged catalyst with repeated intermediate $^{18}O_2$ exchange before choosing another reactant feed. ^{16}O- and ^{18}O-containing products, which were also mainly nitrogen-containing products (NO and NO_2), were monitored with an on-line MS. The reactant concentrations were similar to those used for standard steady-state reactions with helium being the balance to 1 atm.

2.4. *Data treatment for SSITKA*

The raw data obtained from MS was first smoothed using a Fourier Transform algorithm. Subsequently, normalization of the transients was performed by first subtracting the baseline (level of constant minimum intensity) and then dividing every data point of the transient by the maximum intensity of that same

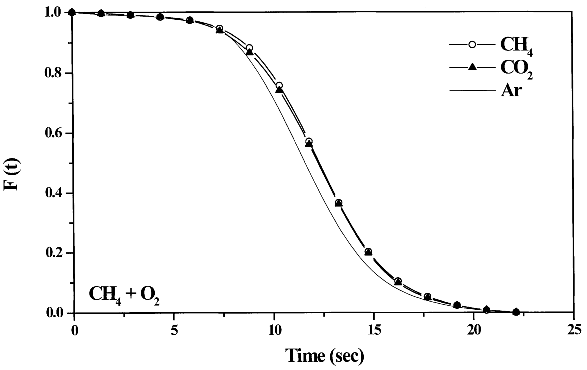

Fig. 1. Typical normalized transients obtained during CH_4+O_2 reaction (reaction (I)) on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 440°C.

transient. The data is plotted as the normalized gas phase concentration of a species, $F(t)$, as a function of time after the isotope switch. Figs. 1 and 2 show decay curves for CH_4 and CO_2 obtained during reactions (I) and (II), respectively, on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 440°C. Since the traces of non-labeled and labeled species were perfectly symmetrical, only decay curves are plotted. Average surface lifetimes (τ) for all species of interest ($^{12}CH_4$, $^{13}CH_4$, $^{12}CO_2$, $^{13}CO_2$, ^{14}NO, ^{15}NO, $^{14}N_2$, $^{15}N_2$, $^{14}NO_2$, and $^{15}NO_2$) were calculated by integrating the area between the transient of each particular species and that of the inert gas tracer (Ar or Ne) which corresponds to the gas phase hold-up. Average site activities were calculated by taking the reciprocals of the surface lifetimes, $k_i = 1/\tau_i$. The surface concentration of labeled intermediates was calculated according to: $N_i = \tau_i FCS/W$, N_i being the surface concentration of labeled products ($\mu mol\,g^{-1}$), τ_i, the surface lifetime of labeled products (s), F, the flow rate of CH_4 or NO ($\mu mol\,s^{-1}$), C, the conversion of CH_4 to CO_2 or of NO to N_2, S, the selectivity towards products, and W, the catalyst weight (g). More information regarding the calculations can be found in [18,19].

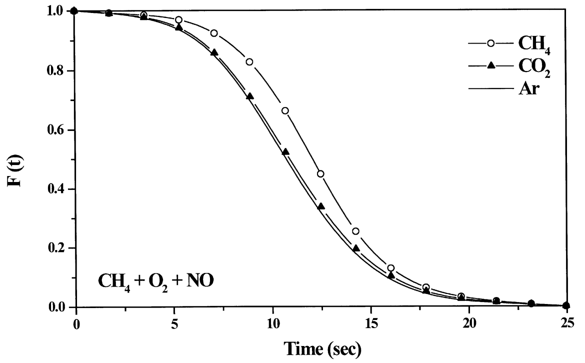

Fig. 2. Typical normalized transients obtained during CH_4+O_2+NO reaction (reaction (II)) on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 440°C.

3. Results

The BET surface areas of the catalysts and the phases in the catalysts determined by XRD are compiled in Table 1. The XRD patterns for Pd-supported hexaaluminates showed trace amounts of metallic Pd (1 1 1) phase. This phase was more pronounced on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ than $Pd/LaMnAl_{11}O_{19}$. Reflections due to PdO could not be identified separately due to the overlapping broad peaks from hexaaluminate phase. Since the catalysts were calcined at 1200°C, possible present phase of PdO was transferred into metallic Pd. Similar observation was also made by Sekizawa [11].

3.1. Steady-state reactions

Steady-state results obtained from system 1 are given in [16]. Focus will be given on the results obtained from system 2. Methane oxidation in the presence of NO was carried out with varying NO concentration. Fig. 3 shows the conversion of CH_4 to

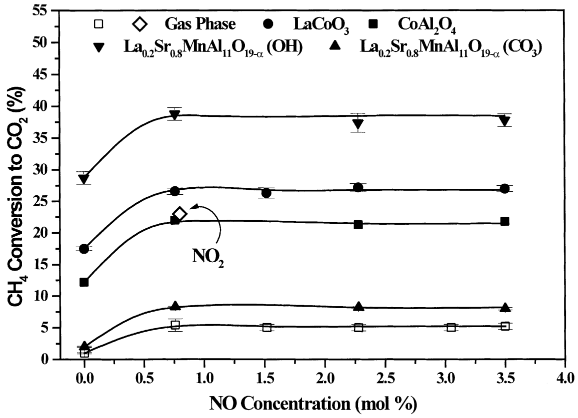

Fig. 3. Methane oxidation activity vs NO concentration. CH_4 and O_2 concentrations are 2.4 and 6%, respectively, with a total flow rate of 33 cc min^{-1}; empty reactor volume was approximately 3 cc.

CO_2 as a function of the NO concentration at 700°C. Addition of even small amounts of NO resulted in an increase in CH_4 conversion. Above a partial pressure of 8 mbar (0.8%) NO, CH_4 conversion to CO_2 was of zeroth order with respect to NO concentration. This behavior was also observed for the non-catalyzed gas phase reaction in an empty reactor. When the same amount of NO_2 (instead of NO) was introduced to the non-catalytic reaction (I), a significant increase in the rate of methane conversion was also observed. In terms of relative amounts, the increase in the rate of methane conversion was the highest in the absence of a catalyst (80% increase) and gradually decreased with increasing conversions on various catalysts. For example, over $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3) catalyst, the effect of NO was only observed at conversions below 3%. At 600°C, however, no difference was observed between reactions (I) and (II), regardless of CH_4 conversion.

In order to determine the exact temperature at which this rate increase begins to occur, reaction (I) was first carried out over $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3), $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (OH), and $LaMnAl_{11}O_{19}$ catalysts at temperatures between 400 and 700°C. After subsequent cooling of the reactor to 400°C, reaction (II) was conducted in the same way. Fig. 4 shows the conversion of CH_4 to CO_2 as a function of temperature over $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3). In a separate set of experiments, these reactions were also carried out over $LaCoO_3$ (perovskite) and $CoAl_2O_4$ (spinel). For all the catalysts tested, the increase in the methane conversion upon NO addition occurred above 650°C. Fig. 5 shows the same data depicted as an Arrhenius plot. Below 620°C, the energy of activation for methane combustion is essentially the same, approximately 102 kJ mol^{-1}, whether or not NO is present. Above ca. 620°C, however, the energy of activation approximately doubled in the presence of NO. For comparison, the apparent energies of activation for methane combustion, with and without added NO, on various catalysts are also compiled in Table 2. All hexaaluminates studied exhibited similar behavior and comparable energies of activation (ca. 100 kJ mol^{-1}). Fig. 6 shows CH_4 conversion to CO_2 over $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3) as a function of reaction time. In order to assess the influence of possible deactivation, the catalyst was monitored for 72 h of reaction time, both with and without NO, during which no deactivation occurred. The variation of reactant partial pressures of CH_4 and O_2 during reaction (II) at 600°C yield reaction orders of 0.9 and 0.6 for CH_4 and O_2, respectively.

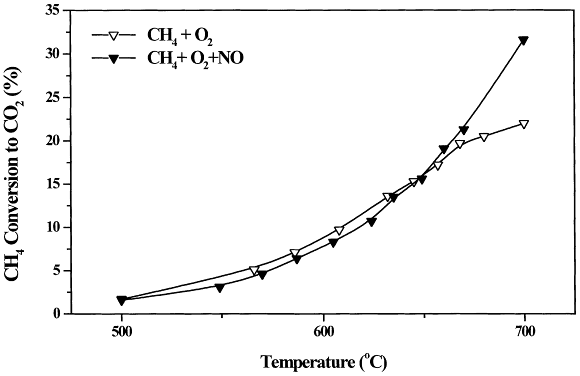

Fig. 4. Methane oxidation activity during CH_4+O_2 (I) and CH_4+O_2+NO (II) reactions on $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3). The reactant concentrations are 2.4% CH_4, 2.3% NO, and 6% O_2, with a catalyst loading of 50 mg and a total flow rate of 33 cc min^{-1}.

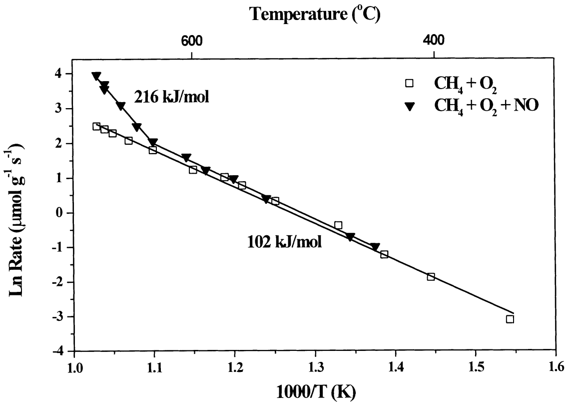

Fig. 5. Arrhenius plot obtained on $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3) for CH_4+O_2 (I) and CH_4+O_2+NO (II) reaction. The reactant concentrations are 2.4% CH_4, 2.3% NO, and 6% O_2, with a catalyst loading of 10 mg and a total flow rate of 33 cc min^{-1}.

3.2. *Steady-state reactions on Pd-doped hexaaluminates*

Fig. 7a and b shows CH_4 conversion to CO_2 over Pd/$LaMnAl_{11}O_{19}$ and Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$, respectively. Pd-impregnated catalysts showed higher combustion activity and a different behavior than

Table 2
Activation energies E (kJ mol^{-1}) for reactions of CH_4+O_2 and CH_4+O_2+NO on various catalysts

Catalysts	Methane combustion			Temperature range (°C)
	CH_4+O_2 (run 1)	CH_4+O_2+NO (run 2)	CH_4+O_2 (run 3)	
$La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3)	102	104	101	375–600
	98	216	–	600–700
$La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (OH)	94	95	97	360–625
$LaMnAl_{11}O_{19}$	89	94	92	375–620
Pd/$LaMnAl_{11}O_{19}$	66	106	68	315–465
$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$	95	98	–	315–580
Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$	75	100	78	320–520

the undoped catalysts towards reactions (I) and (II). In both cases, the rate of CH_4 conversion to CO_2 was first suppressed by NO addition up to a certain temperature (410–450°C). Above this temperature, however, an increase in the rate of CH_4 conversion to CO_2 was noted upon addition of NO.

It was shown in a separate study [20] that the presence of NO during methane combustion on $CoAl_2O_4$ spinel led to irreversible deactivation on the catalyst, most probably caused by surface rearrangement due to oxidation of Co^{2+} by NO. In order to determine whether or not the presence of NO had a similar effect on the hexaaluminate catalysts, they were also subjected to a reaction cycle comprising of (run 1) CH_4+O_2, (run 2) CH_4+O_2+NO, (run 3) CH_4+O_2, and (run 4) CH_4+O_2+NO reaction. Fig. 8a and b shows Arrhenius plots for CH_4 conversion to CO_2 in reaction cycles over $LaMnAl_{11}O_{19}$ and Pd/$LaMnAl_{11}O_{19}$, respectively. The apparent energy of activation remained essentially constant during such a reaction cycle for all non-Pd containing catalysts, whereas the activity pattern was changed upon NO addition over Pd-supported catalysts as described above, but was completely restored to its original value after cutting the NO supply. The apparent energies of activation were around 94 kJ mol^{-1} for $LaMnAl_{11}O_{19}$ for reactions (I) and (II) and 70 kJ mol^{-1} for reaction (I) and 105 kJ mol^{-1} for reaction (II) for Pd/$LaMnAl_{11}O_{19}$. These are further summarized in Table 2. The reversibility of this process on these catalysts suggests the absence of any surface restructuring. This is in contrast with the report of Ribeiro et al. [21] for Pd/Si–Al_2O_3 in the complete oxidation of methane.

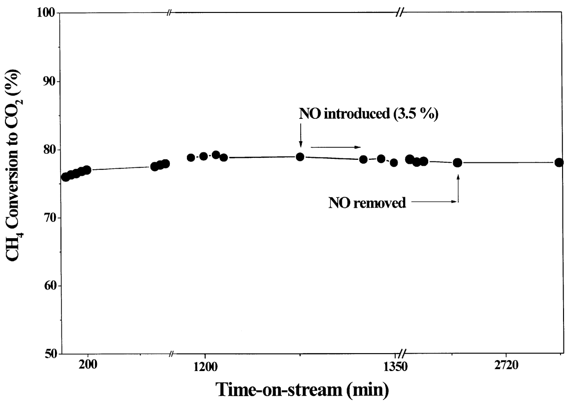

Fig. 6. Methane activity vs time-on-stream on $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3) at 700°C. The reactant concentrations are 2.4% CH_4, 2.3% NO, and 6% O_2, with a catalyst loading of 50 mg, and a total flow rate of 33 cc min^{-1}.

Fig. 9 shows CH_4 conversion to CO_2 and NO conversion to N_2 for reaction of CH_4+NO in the absence and presence of oxygen over $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3) calcined at 1200°C. A significant amount of N_2 was formed in the absence of oxygen. With oxygen addition to the reaction, NO reduction to N_2 was completely suppressed. The apparent energies of activation for NO conversion to N_2 and CH_4 conversion to CO_2 in the absence of oxygen were approximately 120 and 80 kJ mol^{-1}, respectively. The apparent energy of activation for NO reduction by methane on various oxides has been reported to be between 90 and 126 kJ mol^{-1} [22] which is in good agreement with our findings. No homogeneous gas phase reaction between NO and CH_4 was observed at 700°C. Although the rate of combustion was significantly enhanced by NO addition, NO was not reduced to nitrogen in the presence of oxygen.

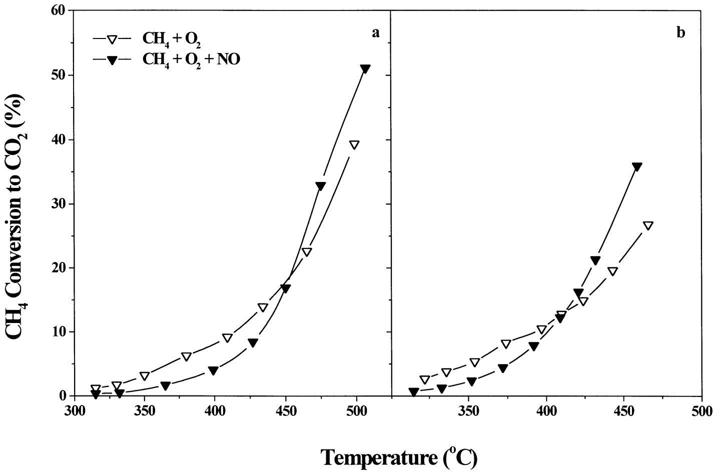

Fig. 7. Methane oxidation activity for CH_4+O_2 (I) and CH_4+O_2+NO reactions on (a) Pd/$LaMnAl_{11}O_{19}$ and (b) Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$, with a catalyst loading of 45 mg, and a total flow rate of 56 cc min^{-1}.

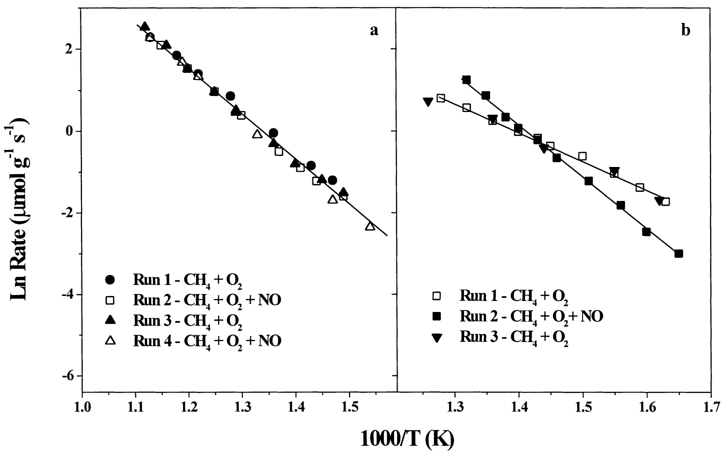

Fig. 8. Arrhenius plots for (a) $LaMnAl_{11}O_{19}$ and (b) Pd/$LaMnAl_{11}O_{19}$ for CH_4+O_2 (I) and CH_4+O_2+NO (II). The reactant concentrations are 2.4% CH_4, 2.3% NO, and 6% O_2, with a catalyst loading of 10 mg (a) and 45 mg (b), and a total flow rate of 56 cc min^{-1}.

3.3. Steady-state isotopic transient kinetic analysis

SSITKA experiments were carried out on selected catalysts based on the results of the steady-state reaction. Table 3 compiles the SSITKA results obtained for Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 360 and 440°C, and for $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 440°C. The rate of CO_2 formation was higher for reaction (I) than that for reaction (II) over Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 360°C. Within the experimental error, the surface lifetime of CH_4 observed for both reactions at 360°C were similar. However, at 440°C a definite increase in the surface lifetime of CH_4 was observed upon NO addition. At 440°C, the rate of CO_2 formation over Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ was higher for reaction (II) than that for reaction (I). A slight decrease in the surface lifetime of CO_2 over Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ was noted at both temperatures upon NO addition. This can be interpreted, in turn, as an increase in the average site activity (turnover frequency) for CO_2 formation. The surface

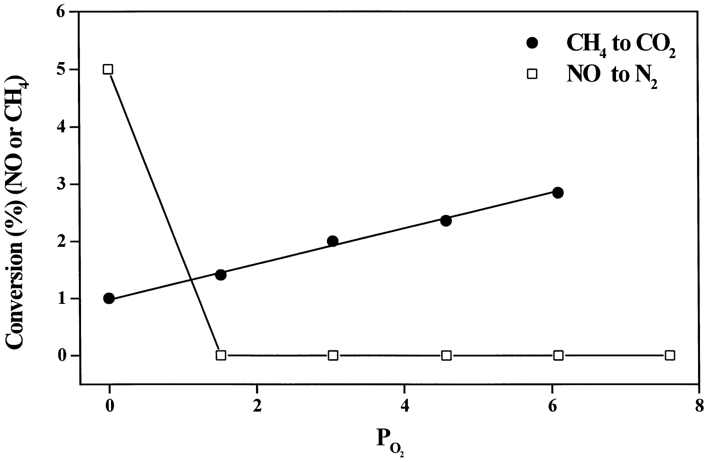

Fig. 9. Methane (to CO_2) and NO (to N_2) conversions vs oxygen partial pressure on $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ at 600°C. The reactant concentrations are 2.4% CH_4, 2.3% NO, and 6% O_2, with a catalyst loading of 50 mg, and a total flow rate of 33 cc min^{-1}.

Table 3
SSITKA results for reactions of CH_4+O_2 and CH_4+O_2+NO on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 360 and 440°C and on $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 440°C, with a catalyst loading of 90 mg and a total flow rate of 56 cc min^{-1}

	Catalysts					
	$Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$				$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$	
	CH_4+O_2 (360°C)	CH_4+O_2+NO (360°C)	CH_4+O_2 (440°C)	CH_4+O_2+NO (440°C)	CH_4+O_2 (440°C)	CH_4+O_2+NO (440°C)
CH_4 conversion to CO_2 (%)	4.5	1.7	14	21	4	4
Rate (μmol g^{-1} s^{-1})	0.31	0.12	0.93	1.5	0.25	0.25
τ_{CH_4} (s)	0.8	0.8	0.5	1.4	0.8	0.9
τ_{CH_2} (s)	0.8	0.5	0.6	0.4	1.4	1.3
k_{CH_4} (s^{-1})	1.25	1.25	2.00	0.71	1.25	1.11
k_{CO_2} (s^{-1})	1.25	2.00	1.67	2.50	0.71	0.77
N_{CH_4} (μmol g^{-1})	5.3	5.3	3.3	9.3	5.3	6.0
N_{CO_2} (μmol g^{-1})	0.2	0.1	0.6	0.6	0.4	0.3

concentration of CO_2 intermediates did not appreciably change when NO was introduced. However, a measurable increase in the surface concentration of CH_4 in the presence of NO was observed at 440°C. In contrast, little differences were observed in surface lifetimes and surface concentrations for the undoped catalysts ($La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$) in the presence and absence of NO (see Table 3). In PTA experiments it was observed that the only ^{18}O-containing nitrogen products were $N^{18}O$ for the NO/He mixture and $^{15}N^{16}O^{18}O$ for the $^{15}NO+O_2$ and $CH_4+^{15}NO+O_2$ mixtures. No $^{15}N^{18}O$ was observed for the $^{15}NO+O_2$ and $CH_4+^{15}NO+O_2$ mixtures.

4. Discussion

4.1. Steady-state reactions on hexaaluminates

When methane combustion was carried out with and without various hexaaluminate catalysts the combustion rate was enhanced by the presence of NO above 650°C. A similar phenomenon has also been reported by Yokoyama and Misono [23]. However, a mechanistic explanation of this enhancement has not been given. It appears that this rate enhancement may be linked to the presence of NO_2 in the gas phase formed by NO oxidation because it was also observed when

NO_2 was substituted for NO in the gas phase without a catalyst. Witzel et al. [24] reported that NO_2 is a more effective oxidizing agent than NO for methane oxidation. They also reported that equal quantity of NO or NO_2 have the same effect on methane oxidation in the presence of O_2, and explained this by the fast equilibration between NO and NO_2 on Co-ZSM5 at their reaction temperatures, between 300 and 500°C. In our work the presence of NO_2 caused a larger increase in the methane combustion rate than that of equivalent amounts of NO, suggesting that equilibration between NO, O_2, and NO_2 did not occur. Indeed, NO_2 and NO would only be equivalent if equilibration occurred fast compared with the actual combustion reaction. This is probably not the case if the reaction occurs in the gas phase and under conditions where CH_4 combustion itself occurs fast [25]. Concentrations of NO above 0.8% did not further increase the methane conversion to carbon dioxide. Li and Armor [26] reported a similar dependence when methane oxidation was carried out in the presence of NO on Co-ZSM-5 catalyst at 400°C, however, an explanation was not given. Our results, as well as those of Lukyanov et.al. [27], suggest that NO_2 is the key element involved in the reaction rather than NO, since the homogeneous gas phase reaction between NO and CH_4 was not observed at temperatures as high as 700°C. The CH_4 conversion to CO_2 appears to be of zeroth order with respect to NO concentration although one would expect to observe an increase in the methane combustion activity with increasing NO concentrations due to the increased formation of NO_2.

Both NO and NO_2 are known to be radical initiators and terminators in chain reactions [28]. It is, thus, conceivable that with increasing NO concentration, more NO_2 is formed, which in turn, accelerates the combustion reaction by oxygen transfer and subsequent radical generation. However, since the equilibrium constant for NO oxidation to NO_2 is small at high temperatures, NO is present in high concentrations thereby acting as a potential radical stopper, resulting in no further increase in the rate for methane oxidation. The rate enhancement upon NO addition can also be seen in the Arrhenius plot (see Fig. 5) obtained with $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO_3) for reaction (II) for which the apparent energy of activation increased from 102 to 216 kJ mol^{-1} above 650°C. This increase of the activation energy with temperature is a clear indication that the rate limiting step of the process has changed in this region. The energy of activation for methane oxidation (with oxygen) in the gas phase was reported to be 202 kJ mol^{-1} [29]. This suggests that at higher temperatures a homogeneous gas phase process may be involved which is not very different from a regular combustion process carried by oxygen.

Numerous reports have been published concerning the selective catalytic reduction (SCR) of NO with methane on zeolites [24,26,27,30,31], on oxidative coupling catalysts, such as La_2O_3 [22,32] and Li/MgO [33], and on alumina-based catalysts [34–36]. On such catalysts, reduction of NO to N_2 in the presence of a hydrocarbon and O_2 was noted. Witzel et al. [24] concluded that the presence of a catalyst is required for this reaction to proceed which assists in the formation of an essential intermediate, such as an aldehyde or ketone [24], or organic nitro compounds [23,37,38]. Since N_2 formation was not observed in the presence of oxygen in the current work, the formation of these essential intermediates on hexaaluminates probably does not occur.

In the presence of both oxygen and NO, methane can react according to [22,30]:

$$CH_4+4NO \rightarrow 2N_2+CO_2+H_2O \quad (1)$$

$$CH_4+2O_2 \rightarrow CO_2+2H_2O \quad (2)$$

Since NO conversion to N_2 was not observed in the present study, reaction (I) can be left out of consideration. However, since the conversion of methane to CO_2 was enhanced by the addition of NO, another route for the formation of CO_2 must exist. Lukyanov et al. [27] reported that CH_4 reacts directly with NO_2 in the gas phase (homogeneously) yielding free radicals at temperatures above 450°C and ultimately forming NO and CO_2 according to the following reaction:

$$CH_4+4NO_2 \rightarrow 4NO + CO_2+2H_2O \quad (3)$$

When the activity of the homogeneous reaction was estimated by extrapolation to 550°C using the rates determined in this work and a value of 216 kJ mol^{-1} for the energy of activation, the rate was determined to be 0.27 μmol min^{-1}. This number is significantly lower than the 1.74 μmol min^{-1} reported by Lukyanov et al. [27] for the overall conversion of methane. If we compare it to their value of 0.46 μmol min^{-1} reported for uncatalyzed homogeneous reaction of methane with NO_2 to CO and CO_2, the figures come reasonably close. The deviation may be attributed to differences in the feed composition and reactor volume, since complete combustion of CH_4 to CO_2 was always noted. More importantly, however, the rate of the catalyzed combustion reaction over $La_{0.2}Sr_{0.8}MnAl_{11}O_{19}$ (CO3) calcined at 1200°C, 2.72 μmol g^{-1} s^{-1} at 550°C, is higher than the extrapolated rate or the value reported by Lukyanov et al. [27]. This explains why the acceleration of the combustion reaction by NO or NO_2 in a homogeneous reaction was only observed above 650°C in our case, as opposed to the observation of Lukyanov et al. [27] of homogenous reaction of CH_4 and NO_2 at 450°C. At higher temperatures, this agrees with the argument made above that NO_2 is directly responsible for initiation of the homogeneous combustion reaction according to [20]

$$CH_4+NO_2 \rightarrow NO + CH_3^* + OH^* \qquad (4)$$

4.2. Reactions on Pd/hexaaluminates

The enhancement in the rate of methane combustion in the presence of NO was observed on Pd-supported catalysts at much lower temperatures, indicating a possible different effect due to the presence of NO or NO_2. In order to elucidate the possible reason(s) for this activity enhancement, Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ was chosen for detailed SSITKA studies. For comparison, $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ catalyst was also studied. Since the contribution of homogenous reactions, presumably due to NO_2, starts above 650°C, the rate enhancement observed on Pd-supported hexaaluminates cannot be simply due to homogeneous reactions. During the NO switches, the products monitored were only NO and NO_2 which co-eluted with the tracer out of the reactor in all cases. Since NO and NO_2 had practically zero surface lifetime (τ), it suggests either no adsorption, an extremely fast adsorption/desorption, or irreversible adsorption of these species. In PTA experiments it was observed that when only NO was passed through the partially ^{18}O-exchanged catalyst, $N^{18}O$ was observed, indicating that NO can adsorb and exchange its oxygen atom on the surface of the catalyst, and can also desorb fairly readily. A number of surface science studies on the adsorption behavior of NO on Pd have shown that the presence of oxygen strongly suppresses NO adsorption and that NO desorbs completely below 350°C [39,40]. When $^{15}NO+O_2$ or $CH_4+^{15}NO+O_2$ mixtures were passed over the partially ^{18}O-exchanged catalyst, the only ^{18}O-containing nitrogen product was $^{15}N^{16}O^{18}O$. It was also observed that there was no $^{15}N^{18}O$ formation, suggesting that in the presence of oxygen, NO does adsorb on the surface and may form NO_2.

As can be seen from Table 3, the surface lifetimes of CH_4 and CO_2 on $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ essentially did not change between reactions (I) and (II) at 440°C. These results demonstrate that the presence of NO had little impact on the conversion of CH_4 to CO_2, i.e., NO did not change the reaction pathway for the CO_2 formation on the catalyst surface. Since the formation of NO_2 was observed, two independent reactions seemed to have occurred on the catalyst, i.e., CH_4 oxidation to CO_2 and NO oxidation to NO_2.

One might consider that NO oxidation to NO_2 may be happening in the gas phase homogeneously. Yokoyama and Misono [23] reported that the conversion of NO to NO_2 was only about 1% for an empty reactor at temperatures between 30 and 500°C with an NO/O_2 ratio of 0.5. As previously mentioned, the homogeneous gas phase reaction between NO_2 and CH_4 becomes important above 450°C [20]. Since the ratio of NO/O_2 used in this work was 0.4, homogeneous gas phase contribution may be neglected at temperatures below 450°C. These results suggest that NO_2 formation can occur on the catalyst surface parallel with the oxidation of methane with oxygen.

The surface concentrations of CO_2 on Pd/$La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ were the same for reactions (I) and (II) at 440°C (see Table 3). Since there was an enhancement in the CH_4 conversion to CO_2, this suggests two different pathways for the formation of CO_2 in the presence and absence of NO. It further suggests that the difference between these reactions occurs due to the presence of Pd in the catalyst. Unlike the case with $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$, NO and/or NO_2 may be participating in the reaction.

Pd metal itself has been reported by various groups to be less active than PdO for the combustion of methane [11–14]. In contrast, Cullis and Willat [41] reported that reduced Pd on alumina is more active at 400°C than the oxidized form. General agreement is that PdO enhances oxygen adsorption, lowering the energy of activation for the combustion of methane

[14]. At temperatures below 800°C, Pd is present in the form of PdO [11,14] in the presence of oxygen. In our case, it is most likely that PdO phase is present in the catalysts since the reactions occur in an oxidizing environment.

SSITKA results for $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ at 440°C show that the surface concentrations of intermediates leading to CO_2 formation are the same whereas the average site activity for CO_2 formation for reaction (II) is slightly higher than that for reaction (I). The latter is further confirmed by the steady-state studies. An increase in k_{CO_2} without a corresponding increase in the surface concentration of reactive intermediates suggests that the presence of NO or NO_2 accelerates the combustion reaction. It is well known that the dissociative adsorption of NO on Pd is suppressed by the presence of oxygen [39,42]. On the other hand, Banse and Koel [43] determined that NO_2 dissociates on Pd surfaces even in the presence of oxygen and leads to higher surface coverage of Pd by oxygen than would be the case if O_2 was used. They attributed this to the higher dissociative sticking coefficient of NO_2 and the lower energy barrier for NO_2 decomposition compared to O_2. These results leave two modes of action open for NO_2 formed via oxidation of NO. It may be that CH_4 is activated on PdO_x surface sites and the surface oxygen is more efficiently replenished by the fast dissociation of NO_2 resulting in faster turnover of intermediates leading to CO_2. Alternatively, during dissociation, NO_2 may deposit activated, more reactive O* species on the surface which themselves may initiate the combustion with methane.

The concentration of methane on the surface increased upon NO addition at 440°C and was higher than that at 360°C. This observation is puzzling at first, since it would suggest an activated adsorption step for methane in the presence of NO. On closer examination, however, a different scenario may take place. Since adsorbed methane represents a precursor to CO_2 formation, one may speculate that not all adsorbed methane, although potentially available, reacts to CO_2. This may better be understood from the following arguments. Once an intermediate is formed from adsorbed methane on the surface, it could decompose (or recombine in the case of radicals) to its original state and desorb as reactant. This appears unlikely, however, because in the presence of NO, active sites are used more efficiently for the formation of intermediates as mentioned above. If the intermediates or radicals formed on the surface were held on the surface one would also expect to observe a higher concentration of the intermediates leading to CO_2, observed as CO_2 in the gas phase, which is not the case for reaction (II). It is, thus conceivable that the intermediates are released to the gas phase in the form of radicals after their formation on the surface and further reactions proceed in the gas phase. Lukyanov et al. [27] also suggested a similar mechanism in which after the radical is produced it may remain on the surface or evaporate into the gas phase. While the radical reactions yielding CO_2 proceed on the surface, reaction of radicals in the gas phase are more prone to be terminated by NO or other radical stoppers such as HNO. Wojciechowski and Laidler [28] reported that the reaction between CH_4 and NO can be terminated according to the reaction

$$CH_3^{*}+HNO \rightarrow CH_4+NO \tag{5}$$

where HNO is an intermediate formed during the chain reactions. Therefore, the higher residence time of methane in the presence of NO at 440°C on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ may indicate that although radicals are increasingly formed, some of them are trapped by radical stoppers and do not react to yield intermediates leading to CO_2.

Similar to the situation at 440°C, the turn over of intermediates leading to the formation of CO_2 was slightly higher at 360°C for reaction (II) than that for reaction (I), suggesting that the presence of NO accelerated the reaction on the active sites. Although the intrinsic rate increased, the total rate, however, decreased upon NO addition. Thus, the concentration of CO_2 intermediates must also decrease in agreement with the results, which are shown in Table 3. Sekizawa et al. [11] and Hicks et al. [44] reported that the methane oxidation reaction is of zero-order with respect to oxygen partial pressure at relatively low temperatures, meaning that oxygen adsorption is fast. Additionally, Riberio et al. [21] reported strong inhibition of H_2O and CO_2 produced during methane oxidation with oxygen on Pd supported on Al_2O_3. Card et al. [45] reported in a TGA experiment that $Pd(OH)_2$ decomposes to PdO at about 247°C when heated in nitrogen. Recently, Giezen et al. [46] reported that H_2O inhibition is present up to 500°C during the methane oxidation reaction on alumina-supported palladium oxide (7.3 wt.% Pd). In our case, any possible water inhibition may not be similar because of very low Pd loading and the hexaaluminate support. Cullis et al. [47] concluded that only relatively large concentrations of water inhibit the oxidation of methane. Since the reactions of methane oxidation in the presence and absence of NO are compared in this paper, it can be assumed that the water inhibition (if exists) may affect the reactions in the same way but does not change the nature of two reactions, CH_4+O_2 and CH_4+O_2+NO. Therefore, this effect can be neglected. Hoost et al. [48] reported infrared studies for NO adsorption on Pd in oxidized and reduced forms of Pd/Al_2O_3. They found that upon heating, linear forms of NO were transferred to bridged forms of NO up to 300°C, the highest temperature measured. NO adsorption on preadsorbed oxygen on Pd/Al_2O_3 also showed that the amounts of bridged NO increased with increasing temperature. Therefore, it is plausible that after NO_2 dissociation on the surface to O* and NO, NO stays on the surface and blocks the accessibility of some of the sites causing the lower number of CO_2 intermediates.

5. Conclusion

Steady-state and SSITKA reactions on $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ suggested that methane and NO oxidation occur on the catalyst surface at 440°C. Steady-state and SSITKA reaction on $Pd/La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ showed that the presence of NO_2 (formed via NO and O_2) boosted the site activity required for the formation of CO_2. In the reaction where NO is involved, NO acts indirectly as chain initiator in the form of NO_2, and also as chain terminator.

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