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Autothermal Oxidative Dehydrogenation of Ethane to Ethylene Using $Sr_xLa_{1.0}Nd_{1.0}O_y$ Catalysts as Ignitors

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The behavior of $Sr_xLa_{1.0}Nd_{1.0}O_y$ catalysts with different Sr loadings ($x = 0$, 0.001, 0.01, 0.1, and 1.0) was examined regarding their application as ignitors for the autothermal oxidative dehydrogenation of ethane. Ethylene yields as high as 42% (S > 69%) were obtained at a contact time of ∼45 ms (STP) as a result of the ignition of the reaction mixture on the catalyst and the resultant occurrence of the thermal ethane pyrolysis. The catalysts showed comparable performance; a slightly higher ethylene yield (45%) was obtained on a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst on which the optimization of the reaction conditions was carried out by varying space velocity ($1 \cdot 10^4$–$8 \cdot 10^4$ h^{-1}), preheat temperature of the feed gas (100–600°C), and ethane-to-oxygen ratio (2–5) in the absence and presence of 15% steam. Space velocity was found to be a significant factor in determining the maximal reaction temperature and hence the extent of thermal pyrolysis. The highest ethylene yield amounted to 56% (S = 71%) achieved at GHSV = $8.3 \cdot 10^4$ h^{-1} ($\tau_{STP} = \sim 45$ ms), $C_2H_6/O_2/N_2 = 2/1/1$, and a preheat temperature of 600°C corresponding to a maximal reaction temperature of 940°C. The addition of steam resulted in some decrease of the maximal temperature leading to a decrease in the ethylene yield by ca. 2%. No significant effect of the steam addition on product distribution was observed.

Key Words: **ethane; oxidative dehydrogenation; Sr–La–Nd–O catalysts; autothermal operation; ignition.**

1. INTRODUCTION

Ethylene is currently produced by the thermal cracking of ethane, ethane–propane mixture, or naphtha (1), which is a highly endothermic and hence energy-intensive process and also involves extensive coke formation. To overcome the problems of thermal cracking, world-wide efforts for the oxidative dehydrogenation of ethane to ethylene (ODE) have been made by many groups; an overview of the results achieved is given elsewhere (2–5). For ODE without the use of halides, different catalytic systems, e.g., V–Mo–Nb–O (6), Li–Mg–O (7), doped rare earth oxides (REO) (8–12), and Pt- and Pt–Sn-coated ceramic foam monoliths (13, 14) were proposed to obtain ethylene yields above 30%.

The development of stable and active catalysts which enable high ethylene yields (>40–50%) and selectivities (>70–80%) is still a challenging task whereby the autothermal operation is preferential due to efficient use of the reaction heat. Schmidt and co-workers (13, 14) reported ethylene yields of 53–57% ($S = 66$–70%) at contact times in the order of milliseconds over Pt-, and Pt–Sn monoliths at 920–925°C in the autothermal mode. Although very high reaction temperatures were used, the influence of the gas phase reaction in the formation olefins was ruled out and a heterogeneous mechanism was proposed. Heterogeneous ignition was achieved by heating the reactants up to ∼230°C (13).

Buyevskaya and Baerns (4, 12) found that catalysts based on REO (Sm_2O_3, La_2O_3, Nd_2O_3) ignite the reaction mixture and allow one to achieve high reaction temperatures (>700°C) without significant external heat input into the reactor. An advantage of the REO-based catalysts is related to their high thermal stability and avoidance of the sintering problem. Although doped REO catalysts were often reported in literature for the ODE reaction (e.g., 8–11), their use as ignitors in the autothermal operation was not proposed before. As shown in Refs. (4, 12), the behavior of REO-based catalysts regarding the ignition of the ethane/oxygen mixture in a fuel-rich regime ($C_2H_6/O_2 \geq 2$) is determined by catalyst activity toward oxygen adsorption and is significantly affected by alkali doping.

The present investigation was undertaken with the objective of evaluating the ignition behavior of Sr–Nd–La–O catalysts with different Sr loading and to examine the effect of different reaction parameters (e.g., space velocity, preheat temperature, C_2H_6/O_2 ratio, addition of steam in the feed) on ethylene formation.

2. EXPERIMENTAL

2.1. Catalyst Preparation and Characterization

The $Sr_xLa_{1.0}Nd_{1.0}O_y$ ($x = 0.0$, 0.001, 0.01, 0.1, and 1.0) catalysts were prepared using nitrates of Sr, La, and Nd

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TABLE 1

Results on the Autothermal ODE Using Different $Sr_xLa_{1.0}Nd_{1.0}O_y$ Catalysts at 860°C (T_{max})

Sr_x loading (mol)	S_{BET} (m^2/g)	$T_{preheat}$ (°C)	Conversion (%) C_2H_6	Conversion (%) O_2	Selectivity (%) C_2H_4	Selectivity (%) CO	Selectivity (%) CO_2	Selectivity (%) CH_4	Selectivity (%) C_{3+}	C_2H_4 Yield (%)
0.0	14.7	375	62.8	100	68.9	10.1	13.2	5.4	2.4	43.3
0.001	13.8	435	60.8	99.8	69.4	9.8	12.6	5.8	2.5	42.2
0.01	23.6	395	60.7	100	69.5	8.3	13.9	6.0	2.4	42.1
0.1	12.7	345	62.4	100	73.0	5.4	12.9	5.6	3.1	45.5
1.0	7.4	340	62.3	100	72.5	5.1	13.1	6.1	3.3	45.1

Note. Reaction conditions: $p(C_2H_6) = 50$ kPa, $C_2H_6/O_2/N_2 = 2/1/1$, GHSV $= 8 \cdot 10^4\ h^{-1}$ ($\tau \sim 45$ ms).

as precursors by citrate methods (15). The main steps were as follows:

(a) preparation of a transparent solution of all components under addition of a small amount of 65% HNO_3 (0.1/250 ml),

(b) addition of citric acid in such a manner that the molar number of equivalent anions is equal to that of the cations,

(c) evaporation of the obtained solution in a Rotavapour under reduced pressure initially at 40–60°C until the solution becomes viscous and then at ca. 90°C until a solid is obtained (amorphous organic precursors),

(d) decomposition of the obtained solids at 380°C for 18 h and finally calcination at 550°C for 6 h.

The surface areas of the catalysts measured by the one-point BET method using Gemini III equipment (Micromeritics) are given in Table 1.

For catalyst $Sr_{0.1}Nd_{1.0}Nd_{1.0}O_x$, which was selected finally for a detailed study, XRD powder analyses were carried out using a STADIP transmission powder diffractometer (Stoe) with $CuK_{\alpha 1}$ radiation. $SrCO_3$, $La_2O_2CO_3$, Nd_2O_3, and La_2SrO_x were the main phases in the fresh samples. After reaction in the absence of steam, no significant change in the above phase composition was detected except the formation of some $La(OH)_3$. The use of steam resulted partially in the transformation of $La_2O_2CO_3$ or Nd_2O_3 into the respective hydroxides. This agrees well with the IR results. In the spectrum of the fresh catalyst, strong adsorption bands at 1400–1600 and at 3600 cm^{-1} were observed which were assigned to the CO_3^{2-} and OH groups, respectively. Under the reaction conditions the concentration of OH groups increased with increasing water partial pressure and the concentration of CO_3^{2-} groups decreased.

2.2. Catalytic Setup and Its Operation

The catalytic reactor along with heating and insulation arrangements used in an autothermal ODE under atmospheric pressure is shown in Fig. 1. The continuous flow quartz reactor ($\varnothing_{in} = 8$-mm catalyst and quartz particle zone; $\varnothing_{in} = 1.75$-mm outlet tube) was packed with 0.3 g (0.18 ml) catalyst ($d_p = 250$–$355\ \mu$m) between two layers of quartz particles of the same size in the zone with an effective cross section of approximately 40 mm^2. The bed length of the quartz particles above and below the catalyst layer for minimizing heat dispersion in the axial directions was 120 and 40 mm, respectively. A thick layer of ceramic wool was used to insulate the outer reactor surface in order to avoid significant radial heat loss. The quartz capillary ($\varnothing_{out} = 3$ mm) containing a movable Chromel–Alumel thermocouple for measuring the temperature profiles was placed into the reactor. The catalyst was charged directly after the preheat zone, which was heated to the desired temperature using heating wire wound around the reactor. The preheat temperature was controlled by an external

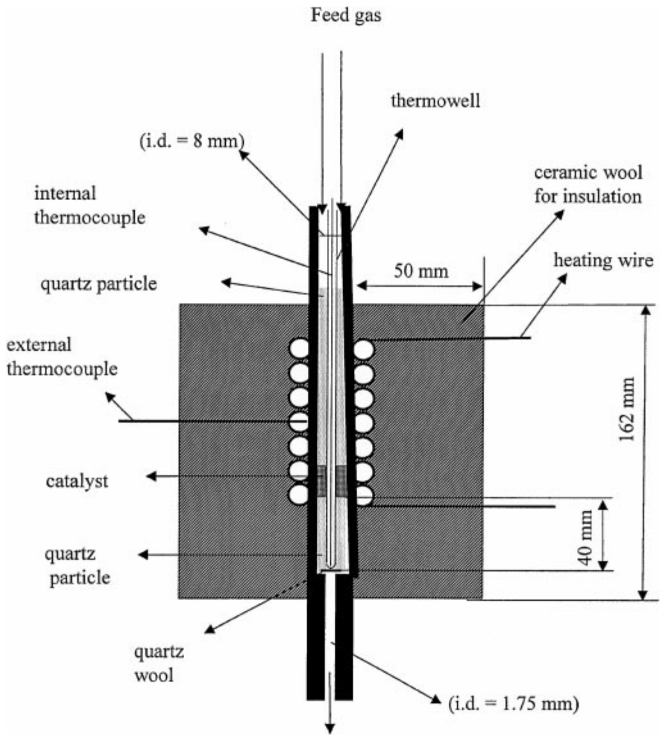

FIG. 1. Tubular quartz reactor along with the heating and insulation arrangements used in an autothermal ODE.

thermocouple. Catalytic experiments were carried out using a mixture of ethane, oxygen, and nitrogen with and without the addition of 15 kPa of steam at different preheat temperatures ($T_{\text{preheat}} = 100$–$600°C$), ethane-to-oxygen ratios (2–5), and flow rates (30–240 ml/min$_{\text{STP}}$); the partial pressure of ethane amounted to 50 kPa in all experiments. Gas hourly space velocity (GHSV) was calculated as the ratio of flow rate to the catalyst volume at standard temperature and pressure. The reactants were fed to the reactor at $T_{\text{preheat}} = 200°C$ and heated further (typically up to 300–350°C) to ignite the reaction mixture. After ignition the preheat temperature was adjusted to the desired conditions. High purity ethane, O_2, and N_2 were fed from high-pressure cylinders through stainless steel lines equipped with check valves, filters, and Bronkhorst mass flow controllers. The feed and products were analyzed by an on-line gas chromatograph with thermal conductivity detector and flame ionization detector using Porapak-Q and Molsieve 5 columns.

3. RESULTS AND DISCUSSION

3.1. Behavior of the $Sr_xLa_{1.0}Nd_{1.0}O_y$ Catalyst with Different Sr Loading

The ODE reaction was first carried out using a $C_2H_6/O_2/N_2 = 2/1/1$ mixture and a total flow rate of 240 ml/min in the presence of different $Sr_xLa_{1.0}Nd_{1.0}O_y$ catalysts ($x = 0$, 0.001, 0.01, 0.1, and 1.0). The ignition of the reaction mixture was observed at 320–350°C on all catalysts and the temperature in the reactor rose rapidly within a few minutes up to 800–860°C. Thus, contrary to the alkali doping (12), the addition of SrO to REO does not affect the ignition temperature. No ignition was observed under similar reaction conditions in the absence of the catalyst. To compare the catalyst behavior regarding ethylene formation, the preheat temperature was adjusted to realize a maximal temperature of 860°C in all experiments. Degrees of ethane and oxygen conversion and selectivities to C_2H_4, CO, CO_2 CH_4, and C_{3+} as well as ethylene yields obtained on all catalysts are given in Table 1. Under the applied conditions the catalysts with different Sr loading resulted in similar ethane conversion (61–63%); no differences in selectivities to CO_2, CH_4, and C_{3+} were observed. An increase in Sr content up to $x = 0.1$ led to a slight increase in ethylene selectivity, coinciding with decreasing CO selectivity. The catalyst with Sr loading of 0.1 and 1 showed the best ethylene yields (45%) under the applied conditions. Therefore, detailed investigations on the effect of process parameters related to the autothermal operation have been performed using a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst.

3.2. Effect of Space Velocity

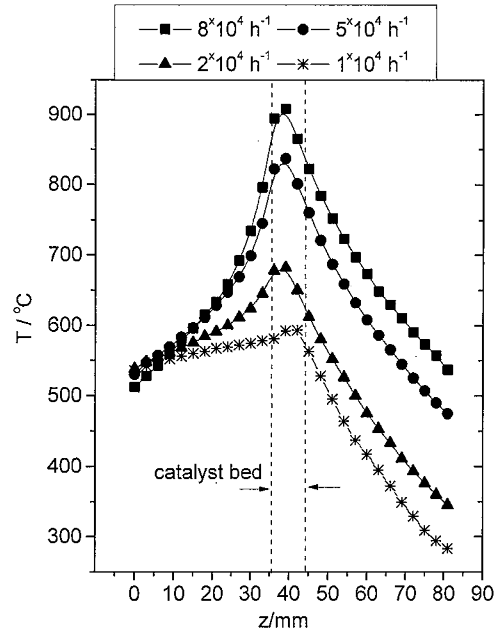

FIG. 2. Temperature profiles in the autothermal reactor after ignition of the reaction mixture on a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst for different space velocities. ($T_{\text{preheat}} = 500°C$, $C_2H_6/O_2/N_2 = 2/1/1$).

Studies on the effect of space velocity were carried over a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst using a $C_2H_6/O_2/N_2 = 2/1/1$ mixture at $T_{\text{preheat}} = 500°C$. Along with the catalytic data the axial temperature profiles in the reactor were measured under steady-state conditions by sliding the internal thermocouple 40 mm upstream and downstream from the center of the catalyst bed. Figure 2 shows that the highest temperature was observed in the catalyst bed for all flow rates; the temperature maximum ($T_{\max}$) was significantly influenced by varying space velocity; a similar observation regarding the reaction temperature in the monolith reactor was reported by Huff and Schmidt (13). An increase in the maximal temperature by more than 300°C was observed on increasing the space velocity from $1 \cdot 10^4$ to $8 \cdot 10^4$ h^{-1}. (cf. Fig. 2).

At temperatures >600°C achieved due to ignition the following main reactions can occur:

$$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O \text{ (exo)} \quad [1]$$

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \text{ (exo)} \quad [2]$$

$$C_2H_6 + 2.5O_2 \rightarrow 2CO + 3H_2O \text{ (exo)} \quad [3]$$

$$C_2H_6 \rightarrow C_2H_4 + H_2 \text{ (endo).} \quad [4]$$

High space velocity causes the release of a large amount of heat in a small catalyst zone due to reactions [1–3]. The drop in the temperature profile is mainly due to the occurrence of an endothermic reaction [4] which can be derived from product distributions as well as oxygen balance (see below). The heat loss was minimized by special insulation but cannot be completely excluded.

Figure 3 shows the influence of space velocity on the conversion of ethane and oxygen, selectivities toward C_2H_4,

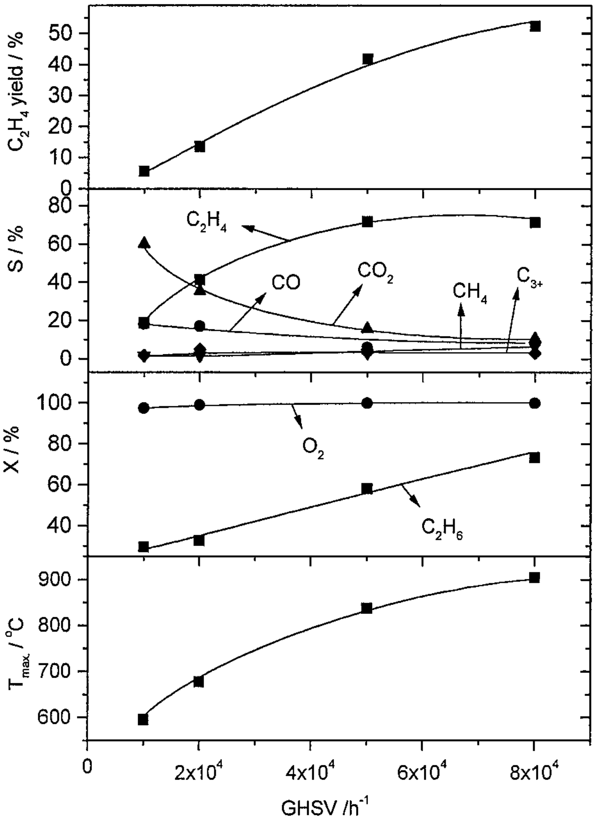

FIG. 3. Effect of space velocity on the conversion of ethane and oxygen, selectivities to C_2H_4, CO, CO_2, CH_4, and C_{3+}, the yield of C_2H_4, and the T_{max} over a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst ($T_{preheat} = 500°C$, $C_2H_6/O_2/N_2 = 2/1/1$).

CO, CO_2, CH_4, and C_{3+}, yield of C_2H_4, and temperature maximum (T_{max}). Total oxygen conversion was achieved in all experiments; the conversion of ethane, ethylene selectivity, and yield as well as T_{max} in the catalyst bed increased whereas the selectivity for CO_2 and CO decreased with increasing space velocity. This indicates that nonoxidative dehydrogenation (Eq. [4]) prevails at high temperatures achieved by increasing space velocity at a constant preheat temperature. At GHSV $= 8 \cdot 10^4$ h^{-1}, an ethylene yield of 53% ($S = 72\%$) was obtained. Lower space velocity led to lower ethylene yields due to lower maximal temperatures at which the extent of thermal pyrolysis decreases.

3.3. Effect of Preheat Temperature in the Presence and Absence of Steam

Results on the degree of ethane and oxygen conversion, selectivity to C_2H_4, CO, CO_2, CH_4, and C_{3+}, yield of C_2H_4, and maximal temperature (T_{max}) in the autothermal ODE using a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst, $\tau \sim 45$ ms, and $C_2H_6/O_2 = 2$ at different preheat temperatures in the presence and absence of 15% steam are presented in Table 2. For both reaction mixtures with and without steam addition, T_{max}, conversion of ethane, and ethylene yield increased with increasing preheat temperature; oxygen conversion was complete in all experiments. Some increase in CO selectivity occurred with increasing preheat temperature whereas selectivity to CO_2 decreased. CH_4 selectivity increased to a small extent, however, the selectivity for C_{3+} remained unaffected with an increase in preheat temperature. No changes in CO and CO_2 formation were observed while adding steam, which indicates that the contribution of the water–gas-shift reaction is not significant in the ODE on REO-based catalysts. The highest ethylene yield amounted to 56% ($S = 71\%$) and was achieved at a preheat temperature of 600°C ($T_{max} = 940°C$ in the catalyst bed). A high reaction temperature (T_{max} in the catalyst bed) obtained by increasing the preheat of the autothermal reactor led to the additional ethane conversion by thermal pyrolysis: $X(C_2H_6)$ increased from 62 to 79% upon enhancing $T_{preaheat}$ from 300 to 600°C; ethylene selectivity slightly decreased due to the formation of more CH_4 at high temperatures.

A comparison of results (Table 2) in the absence and presence of steam shows that ethane conversion and ethylene yield are lower by 4–5 and 2–4%, respectively, in the presence of water over the range of preheat temperature used, this due to the decrease in T_{max} in the presence

TABLE 2

Effect of Preheat Temperature in the Absence and Presence of Steam in the Feed Gas over a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ Catalyst

			Conversion (%)				Selectivity (%)										C_2H_4 Yield (%)	
T_o	T_{max} (°C)		C_2H_6		O_2		C_2H_4		CO		CO_2		CH_4		C_{3+}			
(°C)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
300	852	819	62.0	58.1	100	99.5	73.1	72.2	5.7	4.9	13.8	15.7	4.1	3.9	3.4	3.4	45.3	41.9
400	888	856	67.2	61.8	100	99.8	73.5	73.1	5.9	4.6	12.0	13.9	5.4	5.3	3.2	3.1	49.4	45.1
500	918	888	73.6	70.0	100	100	72.3	72.2	7.4	6.0	10.7	12.1	6.6	6.6	3.1	3.2	53.2	50.5
600	940	899	79.2	79.0	100	100	70.8	68.9	9.4	9.6	9.3	10.1	7.6	7.4	3.0	4.0	56.1	54.4

Note. (a), In the absence of steam: $C_2H_6/O_2/N_2 = 2/1/1$, GHSV $= 8 \cdot 10^4$ h^{-1}; (b), in the presence of steam: $C_2H_6/O_2/N_2/H_2O = 10/5/1/3$, GHSV $= 8 \cdot 10^4$ h^{-1}.

of water. Thus, water does not show any beneficial effect regarding ethylene formation and can be considered an inert dilution in the autothermal ODE on REO-based catalysts. Although hydroxyl groups are formed on the surface in the presence of steam, the hydroxyl groups do not participate in the surface catalysis.

The ethylene yield of 57.4% ($S = 70\%$) was reported by Huff and Schmidt (13) when using a total feed flow rate of 4.5 standard liters per min ($\tau < 10$ ms) at $C_2H_6/O_2 = 1.7$ over the 2.3 wt% Pt-coated ceramic foam monolith at 920°C in an autothermal reactor at a pressure of 1.4 atm. The results in Table 2 show that similar ethylene yield (56%) and selectivity (71%) can be achieved using a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst and a total feed flow rate of 240 ml/min ($\tau \sim 45$ ms) at $C_2H_6/O_2 = 2.0$ and $T_{max} = 940°C$ at atmospheric pressure. The reaction was carried out at several hours without any deactivation.

3.4. *Effect of the C_2H_6/O_2 Ratio*

Figure 4 shows the effect of the ethane-to-oxygen ratio on the degree of conversion of ethane and oxygen, selectivities to C_2H_4, CO, CO_2, CH_4, and C_{3+}, ethylene yield, and T_{max} using a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst, $\tau \sim 45$ ms, and preheat temperature of 390°C. Similar to the effect of space velocity, an increase of oxygen content in the feed resulted in a higher heat production caused in this case by higher ethane conversion in reactions [1–3]. As a result, the temperature in the reactor increased significantly with decreasing C_2H_6/O_2 ratio, allowing the occurrence of thermal pyrolysis to a higher extent. Total oxygen conversion was observed for all C_2H_6/O_2 ratios.

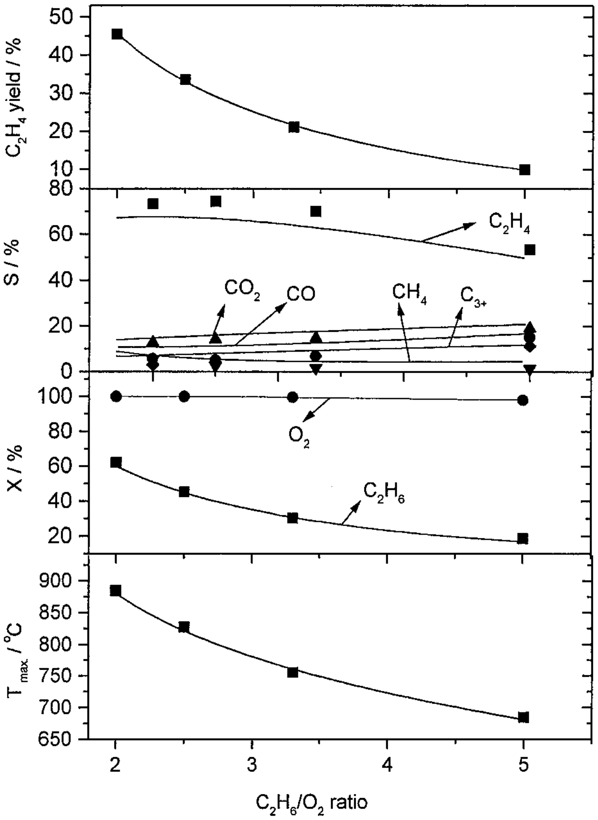

FIG. 4. Effect of ethane-to-oxygen ratio on the conversion of ethane and O_2, selectivities to C_2H_4, CO, CO_2, CH_4, and C_{3+}, the yield of C_2H_4, and T_{max} over a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst ($T_{preheat} = 390°C$, $GHSV = 8 \cdot 10^4\ h^{-1}$, $p(C_2H_6) = 50$ kPa, $N_2 =$ balance).

The conversion of ethane, ethylene selectivity, and yield increased with decreasing C_2H_6/O_2 ratio whereas selectivity for CO, CO_2, and C_{3+} decreased; there is some but not a remarkable increase in the selectivity for CH_4. It is interesting to note that the ignition temperature was not significantly affected by varying the ethane-to-oxygen ratio.

4. CONCLUSIONS

The results obtained in the autothermal ODE using Sr–La–Nd–O catalysts as ignitors reveal that catalytic and noncatalytic reactions occur simultaneously whereby noncatalytic thermal dehydrogenation of ethane proceeds to a great extent at high reaction temperatures obtained by increasing the preheat, space velocity, or oxygen partial pressure. The catalyst acting as ignitor makes possible to decrease the external heat input for sustaining high reaction temperatures at which preferential ethylene formation occurs. Taking into account our earlier findings (4, 12), the following pathways for the formation of desired ethylene can be suggested. The reaction is initiated on the catalyst by formation of ethyl radicals from the surface reaction of ethane with adsorbed oxygen (Eq. [5]):

$$C_2H_6 + [O]_s \rightarrow C_2H_5^{\bullet} + [OH]_s \qquad [5]$$

$$2[OH]_s + 0.5O_2 \rightarrow H_2O + [O]_s. \qquad [6]$$

The ethyl radicals desorb in the gas phase, and their subsequent homogeneous reactions lead to the formation of ethylene (Eqs. [7] and [8]):

$$C_2H_5^{\bullet} \rightarrow C_2H_4 + H^{\bullet} \qquad [7]$$

$$C_2H_6 + H^{\bullet} \rightarrow C_2H_5^{\bullet} + H_2. \qquad [8]$$

At the higher temperatures obtained by increasing space velocity, preheat, and oxygen partial pressure the reaction can be also initiated by the formation of ethyl radicals from ethane:

$$C_2H_6 \rightarrow C_2H_5^{\bullet} + H^{\bullet}. \qquad [9]$$

The thermal decomposition of ethyl radicals (Eq. [7]) and ethane (Eq. [9]) is highly endothermic ($\Delta Hr = 36.4$ and 100.6 kcal mol^{-1}, respectively) and predominant at higher temperatures.

The catalyst acts as an ignitor for the gas-phase radical processes to achieve high ethane conversion and ethylene yield. High space velocity and oxygen partial pressure result in high temperatures in the reactor and favor ethylene formation by thermal dehydrogenation of ethane or ethyl radicals. Ethylene yields of 50–56% ($S = 71$–73%) can be achieved at a short contact time of 45 ms and $C_2H_6/O_2 = 2$ using a $Sr_{0.1}La_{1.0}Nd_{1.0}O_x$ catalyst for ignition. The ethylene yields obtained in the present study are comparable with the present technology for the production of ethylene by thermal cracking; however, ethylene selectivity is lower by 10%. Small reactor volume due to contact times in the millisecond range, high energy efficiency, and catalyst stability are advantages of the autothermal ODE using REO-based catalysts as ignitors. The improvement in ethylene selectivity as well as ethylene yield is a further aim of the optimization studies.

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