Partial Oxidation of Methane to Syngas Using Lattice Oxygen of La$_{1-x}$Sr$_x$FeO$_3$ Perovskite Oxide Catalysts Instead of Molecular Oxygen

Ranjia Li, Changchun Yu, Shikong Shen*

Key Laboratory of Catalysis, China National Petroleum Corporation, University of Petroleum, Beijing 102249, China

[Manuscript received July 30, 2002; revised November 8, 2002]

Abstract: Catalytic partial oxidation of methane to syngas using the lattice oxygen of La$_{1-x}$Sr$_x$FeO$_3$ perovskite oxide catalysts in place of molecular oxygen was studied. La$_{1-x}$Sr$_x$FeO$_3$ ($x=0, 0.1, 0.2, 0.5$) perovskite oxides were prepared by the "auto-combustion method". XRD analysis showed that all La$_{1-x}$Sr$_x$FeO$_3$ samples have a single-phase perovskite-type oxide. The redox properties of the catalysts were investigated by temperature programmed reduction with hydrogen (H$_2$-TPR). Reducibility of the catalysts increase with the increasing of the Sr$^{2+}$ content. The oxygen species of the catalysts and their reaction with CH$_4$ were studied by the temperature programmed surface reaction (CH$_4$-TPSR). In the absence of gas phase oxygen, there exist two kinds of oxygen species on the catalysts. One kind of the oxygen species with strong oxidative ability is produced first, which can oxidize CH$_4$ completely to CO$_2$ and H$_2$O. Then, the second oxygen species with weak oxidative ability is formed, which can oxidize CH$_4$ partially to CO and H$_2$ with high selectivity. The number of the oxygen species with strong oxidative ability in the CH$_4$-TPSR tends to become zero at low x values ($x \leq 0.1$). Under suitable reaction conditions, switching alternatively the reactions of 11% O$_2$-Ar and 11% CH$_4$-He over a La$_{0.8}$Sr$_{0.2}$FeO$_3$ catalyst at 900 °C allows methane to be selectively converted to synthesis gas (CH$_4$ conversion ~90%, CO selectivity >93%) using the lattice oxygen of the perovskite oxide catalyst in a redox mode.

Key words: methane, La$_{1-x}$Sr$_x$FeO$_3$, perovskite oxide, lattice oxygen, partial oxidation, synthesis gas

1. Introduction

Natural gas consists primarily of methane. Since methane is very stable, it is difficult to convert methane into chemical products directly. Synthesis gas production from methane is an important route for the chemical utilization of natural gas, such as for producing methanol, liquid hydrocarbons, ammonia and dimethyl ether [1]. The production of synthesis gas by steam reforming is a process of high energy consumption, and about 60% of the cost of the overall chemical production process goes to synthesis gas generation by steam reforming [2]. Catalytic partial oxidation of methane to synthesis gas, on the other hand, is an attractive route with many advantages when compared to steam reforming, such as having a ratio of H$_2$/CO of 2, higher energy-efficiency and higher selectivities to CO and H$_2$, etc. [3]. Synthesis gas with a hydrogen to carbon monoxide ratio of 2:1 is more suitable for F-T and methanol synthesis. However, the process of catalytic partial oxidation of methane to synthesis gas has not yet been commercialized. Major engineering problems still exist, such as the presence of a high temperature gradient and the risk of explosion, since the premixed CH$_4$/O$_2$ mixtures are within the ignition and explosion limits. The
need for pure oxygen is also another major drawback of this process. The catalytic partial oxidation process must use pure oxygen rather than air to avoid dilution of the synthesis gas by inert nitrogen, and this affects the downstream Fischer-Tropsch or other chemical synthesis processes [4]. Moreover, oxygen supply by the cryogenic distillation of air needs additional investment and operational expenses. To avoid the above problems, intense efforts have been made to use membrane reactors for the partial oxidation of methane to synthesis gas [4–8]. In a membrane reactor, methane and air flow on opposite sides of the membrane, and methane is oxidized to gases by lattice oxygen supplied from the air side of the membrane [4]. Consequently, there is no nitrogen in the product gases. However, there are many practical problems to be solved, for example, reactor scaling up and sealing, before industrial applications of membrane reactors can be realized.

In this paper, a two-step catalytic partial oxidation process is proposed. By using proper oxides as the oxygen source, synthesis gas can be generated from methane and air. In this process a suitable oxide catalyst is circulated between two reactors. In one reactor, methane is oxidized to synthesis gas by the lattice oxygen of the oxide, and in the other reactor, the reduced oxide is re-oxidized by air. Since the reaction occurs between methane and lattice oxygen in the absence of molecular oxygen, this process does not have the risk of explosion and there is no need to supply pure oxygen.

Perovskite-type oxides with the general formula $\text{ABO}_3$, where A and B are metals in the 12- and 6-coordinated sites respectively, have been widely studied as catalysts in the recent years due to their high activity, thermal stability and good performance [9]. Generally, the catalytic activity of perovskite-type oxides is determined by the B cations, and the effect of the nature of the B cations (Fe, Mn or Co) on the catalytic properties of La-based perovskites has been widely studied in methane combustion [9–11]. Substitution of La$^{3+}$ with cations of a lower oxidation state leads to the formation of oxygen vacancies and/or a fraction of the B cations in a higher valence state [12–15], which results in perovskite oxides with a better catalytic activity.

This work reports on the preparation and characterization of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ $(x=0, 0.1, 0.2, 0.5)$ perovskites, and the influence of the substitution of Sr$^{2+}$ for La$^{3+}$ on methane partial oxidation to syngas by using the lattice oxygen of the perovskite oxides in the absence of molecular oxygen.

2. Experimental

2.1. Catalyst preparation and pretreatment

The perovskite oxide $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ $(x=0, 0.1, 0.2, 0.5)$ catalyst was prepared by an auto-combustion method [16, 17]. A concentrated solution of the metal nitrates was mixed with an aqueous solution of glycine with a ratio of $\text{NH}_3/\text{NO}_3=1.05$. Water was slowly evaporated from the mixed solution at 70 °C until a viscous gel was obtained. The gel was then kept at 250 °C for 30 min, during which a fast reaction took place, forming a pulverous precursor. The catalyst precursor was then calcined at 900 °C for 4.5 h. The samples were crushed, ground and sieved prior to testing. Before characterization, the catalyst was treated in flowing air (25 ml/min) by heating at 10 °C/min from room temperature to 900 °C and held at this temperature for 15 min, and then cooled to room temperature.

2.2. Characterization

Crystal phase analysis was performed by powdered X-ray diffraction (XRD) on a SHIMADZU XRD-6000 diffractometer using Cu $K_\alpha$ radiation.

Temperature programmed reduction with hydrogen (H$_2$-TPR) and temperature programmed surface reaction with methane were performed in a fixed-bed quartz micro-reactor (4.5 mm ID) loaded with 150 mg of catalyst sample. An on-line quadrupole mass spectrometer (AMTEK Q200MN) was used to monitor the products from the reactor. The quadrupole mass spectrometer can detect eight mass channels simultaneously with a minimum dwelling time of 3 ms. H$_2$-TPR was carried out from room temperature to 900 °C at a heating rate of 15 °C/min. The reducing or reaction mixture was 12 mol%H$_2$/He or 10 mol%CH$_4$/Ar.

2.3. Switching reaction between CH$_4$ and O$_2$

In order to simulate a redox cycle, switching reactions between a flow of 11 mol% O$_2$/Ar and a flow of 11% CH$_4$/He at 900 °C were performed. The total gas flow rate was 23 ml/min. Ar/He was used as dilution gas and tracer gas.
3. Result and Discussion

3.1. XRD characterization

Pevovskite-structured oxides have the general formula of ABO₃, where the 12-coordinated (AO₁₂) A sites may be occupied by large ions (rₐ > 0.090 nm, usually a rare-earth metal) and the 6-coordinated (BO₆) B sites are usually occupied by transition metal cations (rₐ > 0.051 nm). Furthermore, the tolerance factor t of a perovskite compound \[ t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \] must be in the range of 0.75–1.0 [18]. For the La₁₋ₓSrₓFeO₃ compound series, the t values are listed in Table 1. All t values of the La₁₋ₓSrₓFeO₃ (x=0, 0.1, 0.2 and 0.5) oxides are in the range of 0.75–1.0. Thus, it is possible for the catalysts with these compositions to form a perovskite structure.

Table 1. Tolerance factors of the La₁₋ₓSrₓFeO₃ series catalysts

<table>
<thead>
<tr>
<th>x</th>
<th>Tolerance factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.957</td>
</tr>
<tr>
<td>0.1</td>
<td>0.960</td>
</tr>
<tr>
<td>0.2</td>
<td>0.962</td>
</tr>
<tr>
<td>0.5</td>
<td>0.971</td>
</tr>
</tbody>
</table>

The XRD patterns of the La₁₋ₓSrₓFeO₃ oxide series with x=0, 0.1, 0.2 and 0.5 are given in Figure 1. A comparison with the XRD data of the perovskite-structured oxide LaFeO₃ (JCPDS card No.37-1493) shows that the XRD patterns of the catalysts are similar, and they can be considered as perovskite structures, with part of the La substituted by Sr. Figure 1 clearly shows that the X-ray diffraction lines are continuously shifted to higher θ values with the increase of x. According to the Bragg’s Equation, this behavior means that the unit cell parameters decrease with the increasing of the Sr content.

3.2. Temperature programmed reduction by hydrogen (H₂-TPR)

Temperature programmed reduction results of the La₁₋ₓSrₓFeO₃ (x=0, 0.1, 0.2, 0.5) catalyst series by 12 mol H₂/He are listed in Table 2 and Figure 2.

Table 2. The amount of hydrogen consumed by La₁₋ₓSrₓFeO₃ in H₂-TPR

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>First peak</th>
<th>Second peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum temperature (°C)</td>
<td>Hydrogen amount (µmol/g)</td>
</tr>
<tr>
<td>LaFeO₃</td>
<td>–</td>
<td>78.5</td>
</tr>
<tr>
<td>La₀.₉Sr₀.₁FeO₃</td>
<td>408</td>
<td>280.9</td>
</tr>
<tr>
<td>La₀.₈Sr₀.₂FeO₃</td>
<td>426</td>
<td>390.3</td>
</tr>
<tr>
<td>La₀.₅Sr₀.₅FeO₃</td>
<td>455</td>
<td>995.7</td>
</tr>
</tbody>
</table>

Hydrogen consumption by the LaFeO₃ catalyst is very low in the temperature range from 150 °C up to 900 °C. However, two obvious hydrogen consumption peaks are observed for samples with x≥0.1. The samples with substituted Sr undergo reduction starting at low temperatures and the amount of hydrogen consumption increases greatly with the Sr content. With an increase in Sr content, the maximum temperature of the first peak increases and the starting temperature of the second peak decreases. The temperature
range of the first peak tends to broaden with the Sr content.

To keep a balance of the charge, the La$_{1-x}$Sr$_x$FeO$_3$ catalysts can be changed in one or both of two ways after part of the trivalent lanthanum ions has been substituted by lower valence bivalent strontium ions. The first way is the formation of oxygen vacancies in the Sr-containing catalysts. The second one is the oxidation of a fraction of the Fe$^{3+}$ to a high valence state (Fe$^{4+}$) [14]. The redox reaction between Fe$^{4+}$ and Fe$^{3+}$ in the B sites in the Sr$^{2+}$ substituted La$_{1-x}$Sr$_x$FeO$_3$ catalyst is relatively easy. Thus, the La$_{1-x}$Sr$_x$FeO$_3$ catalysts can provide much more oxygen than pure LaFeO$_3$ at lower temperatures. In the La$_{1-x}$Sr$_x$FeO$_3$ catalyst series, the Fe$^{4+}$ content will increase with increasing of the Sr content, and results in an increase in hydrogen consumption, as reflected in the first peak of the H$_2$-TPR [15].

Figure 2. H$_2$-TPR of La$_{1-x}$Sr$_x$FeO$_3$.

x: (1) 0, (2) 0.1, (3) 0.2, (4) 0.5.

Figure 3 shows the XRD patterns of the La$_{1-x}$Sr$_x$FeO$_3$ catalyst series after H$_2$-TPR. It can be seen that the La$_{1-x}$Sr$_x$FeO$_3$ catalysts with a small amount of the La$^{3+}$ substituted by Sr$^{2+}$ (x=0.1, 0.2) still have the perovskite structure. However, besides the perovskite structure, the La$_2$O$_3$ structure pattern appears in the La$_{0.5}$Sr$_{0.5}$FeO$_3$ catalyst after H$_2$-TPR to 900 °C. Interestingly, if H$_2$-TPR of the La$_{0.5}$Sr$_{0.5}$FeO$_3$ is stopped at the end temperature of 500 °C of the first peak, the XRD pattern of the catalyst shows that it is a pure perovskite structure. It can be concluded that Fe$^{4+}$ is mostly reduced to Fe$^{3+}$ at temperatures lower than 500 °C, while part of Fe$^{3+}$ is possibly reduced to Fe$^{2+}$ at higher temperatures.

3.3. Temperature programmed surface reaction of methane (CH$_4$-TPSR)

The results of the temperature programmed surface reaction with methane over the La$_{1-x}$Sr$_x$FeO$_3$ catalysts are shown in Table 3 and Figures 4(a) to (d). Figure 4(a) shows that there exist two CH$_4$ consumption peaks in the CH$_4$-TPSR. The temperature range of the first uptake of CH$_4$-TPSR is from 400 °C to 620 °C, while the onset temperature of the second peak is 730 °C. The results indicate that two different oxygen species exist in the La$_{0.5}$Sr$_{0.5}$FeO$_3$ catalyst. According to the product distribution of the two CH$_4$-TPSR
peaks, the oxygen species of the La$_{0.5}$Sr$_{0.5}$FeO$_3$ reacting at lower temperatures corresponding to the first CH$_4$-consumption peak has strong oxidizing ability, and results in the complete oxidation of CH$_4$ to CO$_2$ and H$_2$O, while the high temperature oxygen species reacting at over 730°C has moderate oxidizing ability and mostly results in the selective oxidation of CH$_4$ to CO and H$_2$, so that only a little complete oxidation products of CO$_2$ and H$_2$O is formed.

The results of CH$_4$-TPSR over the La$_{0.8}$Sr$_{0.2}$FeO$_3$ catalyst (Figure 4(b)) are similar to that over the La$_{0.5}$Sr$_{0.5}$FeO$_3$ catalyst. However, the amount of CO$_2$ formed is much lower than that of the La$_{0.5}$Sr$_{0.5}$FeO$_3$ catalyst, and most of the CH$_4$ is selectively oxidized to CO and H$_2$.

With a decrease in the Sr$^{2+}$ content to $x$=0.1, only a very small amount of CH$_4$ is converted and the corresponding CO$_2$ is formed in a lower temperature range in CH$_4$-TPSR (see Figure 4(c) and Table 3). No CH$_4$ consumption and no CO$_2$ formation can be detected over the LaFeO$_3$ catalyst at temperatures lower than 700 °C. A high CH$_4$ consumption peak appears in the high temperature range in CH$_4$-TPSR on both of the La$_{0.9}$Sr$_{0.1}$FeO$_3$ and LaFeO$_3$ catalysts, and the corresponding products are CO and H$_2$, with only small amounts of CO$_2$ and H$_2$O being detected. These results demonstrate that both of the La$_{0.9}$Sr$_{0.1}$FeO$_3$ and LaFeO$_3$ catalysts provide mainly oxygen species with strong oxidative ability, which can oxidize CH$_4$ to synthesis gas with high selectivity.

Figure 4. CH$_4$-TPSR/MS of (a) La$_{0.5}$Sr$_{0.5}$FeO$_3$, (b) La$_{0.8}$Sr$_{0.2}$FeO$_3$, (c) La$_{0.9}$Sr$_{0.1}$FeO$_3$, (d) LaFeO$_3$. (1) CO$_2$, (2) CO, (3) H$_2$O, (4) CH$_4$, (5) H$_2$.
lysists after the CH react with CH
reduce in a H
ature reactive oxygen species is much higher than that
acting in the lower temperature range has strong ox-
idenation. XRD patterns indicate that a
La crystal structure appears in these cata-
3.4. Switching reactions between 11 mol% O2/Ar flow and the 11 mol% CH4/Ar flow over La0.8Sr0.2FeO3

From the CH4-TPSR results of the La1−xSr2FeO3 catalyst series, it can be clearly seen that catalysts with a relatively high Sr content (x = 0.2 and 0.5) have two different kinds of oxygen species; the species reacting in the lower temperature range has strong oxidizing ability, while the oxygen species reacting in the high temperature range has good selectivity for the oxidation of CH4 to synthesis gas. The amount of the lower temperature and strongly oxidizing oxygen species decreases with decreasing Sr content in the La1−xSr2FeO3 catalyst series. This result is in accordance with the H2-TPR experiments.

During H2-TPR and CH4-TPSR, the La1−xSr2FeO3 catalyst is the only oxygen source. According to the amount of hydrogen consumed in H2-TPR and the total amount of the oxygen-containing products produced in CH4-TPSR, the amount of oxygen species provided during CH4-TPSR and H2-TPR can be evaluated. By comparing CH4-TPSR with H2-TPR, the amount of reactive oxygen species provided in CH4-TPSR is more than that in H2-TPR over the same La1−xSr2FeO3 catalyst. However, the amount of oxygen species provided in lower temperature range in CH4-TPSR is less than that in H2-TPR, whilst the amount of the high temperature reactive oxygen species is much higher than that in H2-TPR, especially for high Sr content catalysts. The results show that the catalysts La0.8Sr0.2FeO3, La0.9Sr0.1FeO3 and LaFeO3, which are difficult to reduce in a H2-He atmosphere at high temperatures, can selectively oxidize CH4 to CO and H2 by supplying lattice oxygen. XRD patterns indicate that a new La2O3 crystal structure appears in these catalysts after the CH4-TPSR. Most of the oxygen that reacted with CH4 is provided by the La0.8Sr0.2FeO3, La0.9Sr0.1FeO3 and LaFeO3 catalysts at high temperatures. Meanwhile, part of the Fe3+ and/or Fe2+ is possibly reduced to lower valence iron, and results in a loss of the perovskite structure.

3.4. Switching reactions between 11 mol% O2/Ar flow and the 11 mol% CH4/Ar flow over La0.8Sr0.2FeO3

In order to simulate the partial oxidation of methane to synthesis gas by the lattice oxygen of the La0.8Sr0.2FeO3 catalyst, switching reactions between O2/He and CH4/Ar flows were carried out at 900 °C. The transient switch responses after switching from O2/He (11 mol% O2) to CH4/Ar (11 mol% CH4) over La0.8Sr0.2FeO3 are shown in Figure 5. The results indicate that most of the CH4 is converted to CO2 and only little CO is formed in the initial 8 seconds of the CH4/Ar flow, then the CO2 intensity goes down dramatically and the CH4 intensity goes up sharply. After a 10-second reaction under CH4/Ar flow, CO and H2 appear, and their intensities increase steadily with time, while the CH4 intensity decreases gradually. After CH4/Ar reaction of 60 seconds, CH4, H2 and CO intensities reach their respective steady-state levels and the signal of CO2 disappears. The results illustrate that a pre-oxidized La0.8Sr0.2FeO3 catalyst can provide two kinds of oxygen species. First, the oxygen species with strongly oxidizing ability, which is only a small amount of the total reactive oxygen provided by the catalyst, oxidizes CH4 to CO2 and H2O. Next, after the stronger oxidizing oxygen species is used up, large amount of selective oxygen species reacts with CH4 and produce CO and H2. When CH4 reacts with the La0.8Sr0.2FeO3, this catalyst is the only oxygen source. As the reaction goes on, oxygen will be derived from the pre-oxidized La0.8Sr0.2FeO3 catalyst, which is then gradually reduced. Selective oxygen species can be supplied as the catalyst achieved an appropriate surface state. The results are consistent with that of the CH4-TPSR.

Figure 6 shows the result of the switching reactions from the O2/Ar oxidation for 11 seconds to the CH4/He reaction for 25 seconds repeatedly over
a La$_{0.8}$Sr$_{0.2}$FeO$_3$ catalyst pre-treated under CH$_4$/He for 2 minutes at 900 °C. After pre-reduced by CH$_4$, the catalyst provides mainly selective oxygen species. No significant CO and CO$_2$ were detected when switching from the CH$_4$/He to the O$_2$/Ar flow over the pre-treated La$_{0.8}$Sr$_{0.2}$FeO$_3$ oxide. On switching from O$_2$/Ar to CH$_4$/He, large amount of CO and H$_2$ is formed, while the CO$_2$ intensity remains at its original background level. Calculations show that the CH$_4$ conversion is 90%, H$_2$ and CO selectivities are over 93%, and the ratio of H$_2$/CO is about 1.90 and near the stoichiometric ratio of the partial oxidation of methane. In this way, methane can be converted to synthesis gas with very high conversion and selectivity under the experimental condition, and there is no carbon deposition on the catalysts.

Figure 5. Transient responses from switching O$_2$/Ar flow (11 mol%O$_2$) to CH$_4$/He flow (11 mol%CH$_4$) over La$_{0.8}$Sr$_{0.2}$FeO$_3$ at 900 °C.
Reaction conditions: total flow rate 23 ml/min, catalyst mass 100 mg.

Figure 6. Transient responses of the switching reaction between O$_2$/Ar flow (11 s, 11 mol% O$_2$) and CH$_4$/He flow (25 s, 11 mol%CH$_4$) over pre-treated La$_{0.8}$Sr$_{0.2}$FeO$_3$ catalyst at 900 °C.
Reaction conditions: total flow rate 23 ml/min, catalyst mass 250 mg.
In summary, there are two kinds of reactive oxygen species in La$_{0.8}$Sr$_{0.2}$FeO$_3$, one kind has strong oxidizing ability and is highly active. It reacts rapidly with CH$_4$ to form CO$_2$ and H$_2$O. Another kind is lattice oxygen. This has good partial oxidation selectivity, and can selectively oxidize CH$_4$ to CO and H$_2$. This study also shows that CH$_4$ can be selectively converted to synthesis gas with high conversion under proper reaction conditions. The selective oxidation activity of the catalyst can be recovered by re-oxidation for an appropriate time period using gas phase oxygen. The selective oxidation of methane to synthesis gas can be carried out by a redox process using the lattice oxygen of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ catalyst instead of molecular oxygen.

Acknowledgement

Financial support by China Petroleum & Chemical Corporation (X502015) and The Innovation Foundation of Petroleum Technology CNPC (cx200139) are gratefully acknowledged.

References