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Catalytic activity of Perovskite -based $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ in a packed-bed reactor for partial oxidation of CH_4 using N_2O as an oxidant

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Abstract: Perovskite -based $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ (LSCF3773, LSCF) were used as a catalyst in synthesis gas production via an integration of nitrous oxide decomposition with methane partial oxidation reaction in a packed-bed reactor. LSCF powder was prepared by ethylene glycol modified Sol-gel-Pechini and sintered at 1100°C with slow heating rate in order to complete a pervoskite phase. A crystalline phase and a crystallite size of the synthesized powder were analyzed by x-ray diffraction technique (XRD). Partial oxidation was performed by feeding of CH_4 and N_2O in a packed-bed reactor. CH_4-TPR was applied to investigate the CH_4 absorption behavior on surface and in lattice of catalyst. The result of CH_4-TPR showed that CH_4 consumption occurred during 900°C to 950°C in temperature, and at 920°C was found the highest of CH_4 was oxidized with O_2 on the surface and in the lattice and gave the highest products (H_2 and CO), called methane partial oxidation reaction (POM). In reaction performance, suitable CH_4/N_2O molar ratio and operating temperature for the highest CH_4 conversion at 99.31% and hydrogen (H_2) to carbon monoxide (CO) ratio at 2.07 were achieved when introducing 1.08 molar ratio of CH_4 to N_2O at 950°C. The stability test of LSCF3773 performed 10 hours with a stable activity of catalyst by achieved 99% CH_4 conversion throughout 10 hours and H_2/CO ratio approached to 2 in POM reaction. LSCF3773 was considered as the phase reversibility by XRD after the stability test. The XRD pattern confirmed that the perovskite phase can appear again by full replenishing with O_2 into the lattice, called as the regeneration with O_2 treatment. As a result, LSCF3773 structure can appear again with the perovskite phase and can be renewable as a new catalyst in order to reuse in a new reaction. Therefore, in this work, $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ can meet the objectives in terms of 1.) High CH_4 conversion, 2.) Product selectivity with 2 of H_2/CO ratio, which is dominant with partial oxidation reaction, and 3.) an ability for continuous running for 10 hours for co-feed N_2O and CH_4 at operating condition as 1.08 molar ratio of CH_4 /N_2O at 950°C. 4.) Regenerable property.

Keywords: Perovskite-type material, Synthesis gas production; N_2O decomposition, Partial oxidation of methane.

1. Introduction

Nowadays, a big concern of mankind in the world is a global warming impact resulted from the greenhouse gases (GHG), which emits radiation from the sun by the thermal infrared energy in the atmosphere as well as destroy the ozone layer in the stratosphere [1-2]. The important greenhouse gasses are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and other fluorinated gases [1]. One of significant GHG is N_2O. Nitrous oxide (N_2O) has a harmful impact in GWP more than CO_2 approximately as 310 times and normally, it can be emitted from both natural sources and anthropogenic sources [3-5]. Mainly, N_2O emissions were originated from anthropogenic sources according to the European Environment Agency 2008, it reported about N_2O emissions in EU that 46 % N_2O emitted from agriculture –like fertilized agriculture land, and 28 % N_2O emitted as an undesirable by-product from many chemical industries – such as nitric acid manufacturing, adipic acid, caprolactam, glyoxal, glyoxylic acid production plants etc. [1, 6-7]. In order to reduce N_2O emissions, a N_2O decomposition unit, decomposing N_2O as O_2 and N_2, was made by many industries before releasing to environment. However, this process is as a useless of energy source and according to an attention of developing alternative energy, including to decrease uses of energy from fossil fuels in the future. Instead of just decomposing the N_2O, catalytic partial oxidation of methane using greenhouse gas, nitrous oxide (N_2O) as an oxygen source via N_2O decomposition in a packed-bed reactor could be a good solution. This process will not only eliminate the N_2O, but also to produce energy or chemical intermediates in the form of synthesis gas.

In this study, a co-feed N_2O and CH_4 system of catalytic methane partial oxidation uses N_2O decomposition as a source of oxygen. N_2O was decomposed by using oxygen vacancies (*) and also use absorbed oxygen (O*) on the catalyst surface as active sites [8] and for methane partial oxidation, CH_4 was used as the reducing agent. Thus it can oxidize with absorbed oxygen atom (O*) and oxygen molecule (O_2*) on the surface of catalyst to produce a synthesis gas (H_2 and CO) as product gas. From above mention, the suitable catalyst should provide a good activity for those two reactions, which are N_2O decomposition and CH_4 partial oxidation reaction. In addition to, it should has properties relating to oxygen mobility in lattice and good performance in a redox reaction.

Perovskite oxides type materials, usually studied in N_2O decomposition and partial oxidation, have ideal formular as ABO_3 and were considered as mixed ionic/electronic conducting ceramic materials because I.).A lot of oxygen vacancy II.) Ion-electron can mobile and exchange across the lattice [9-11]. The perovskite ABO_3 contains A-side cation, which is larger ions more than another side or usually use metal ions such as rare earth, alkaline earth, alkali, and also consists of B-side cation-such as transition metal ions [9, 12-15]. This ideal structure can make unstable between A-site and B-site, which results in escaping of oxygen atom in order to balance the perovskite structure and perform non-stoichiometry (δ) in lattice [12-15,xx]. As a consequence, the perovskite material exposes to high ionic and electronic conductivity property. Moreover, to improve electronic and ionic conductivity, perovskite will be modified to be defected lattice structure by introducing a lower valence dopant A' and B' on the A side and B side respectively to form as formula $A_xA'_{x-1}B_yB'_{y-1}O_{3-\delta}$. The symbol δ express the amount of oxygen vacancies (defects). Ion vacancies provide a pathway for ions, therefore the oxygen mobility can be increased by increasing the amount of oxygen vacancies [9, 16-18]. In previous research study, for N_2O decomposition, without a catalyst, it can decompose at temperature above 700°C. Various types of catalysts such as noble metals (Pt, Pd, Ag, Au and Ge), Metal oxides (MgO, NiO, Fe,O,etc.) [7] have been studied in N_2O decomposition to reduce operating temperature and achieve a good conversion of products, However, they have a limitation in terms of high cost, high operating temperature and giving instable property for high temperature. Perovskite-type oxide is one of good candidates to overcome these limitations, lower cost and lower operating temperature, moreover, it performs a stable activity at high temperature. Pan *et al.* [19] presented that 100 % N_2O decomposition with catalyst as La_2NiO_4, $LaSrNiO_4$, $La_{0.7}Ce_{0.3}SrNiO_4$ at 500°C, 600°C, and 600°C respectively. For CH_4 partial oxidation, currently, perovskite materials have widely used as both of reactant and catalyst in partial oxidation reaction. Zhao et al. studied $La_{1-x}Sr_xFeO_y$ (LSF) family as oxygen carriers for partial oxidation. The result shown that partial substitute A-site by Sr with x=0.3 and 0.5 provided the best result for partial oxidation, 70% conversion and 2:1 for H_2/Co ratio. Moreover, they found that $La_{1-x}Sr_xFeO_y$ perovskites have a stable activity and good regenerability by taking O_2 for regeneration after oxidizing with CH_4 for 5 cycles. Moreover, Babiniec et.al. studied partial substitution of Co in B-site such a $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (LSCF), which one of the good candidates for high-temperature redox reactions due to their capability for both endothermic reduction and oxidation, at x=0.3, y=0.7, $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ (LSCF3773) performed the best changes in oxygen non-stoichiometry (Δδ), determined by TGA. LSCF3773 showed the highest $\Delta\delta_3$ at 0.40 which is supposed to provide the best redox property amongst all the $\Delta\delta_3$ [20].Thus, many studied publication studied and accepted that perovskite oxide type based on LSF, LSCF provided a good performance in term of high activity and had stability in high temperature in methane partial oxidation [3, 20-22] , since they possess high oxygen storage and oxygen mobility in the lattice [9, 12-15, 22].

As above mention, in this work, $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ was chosen suitably as a catalyst for both of N_2O decomposition and methane partial oxidation reaction, which is Co-fed N_2O and CH_4 in packed-bed reactor. The expectations of LSCF3773 properties are to achieve : (1) A lot of oxygen vacancy in structure, (2) A good oxygen ability, (3) Cubic structure defining to stable structure of the perovskite [9, 11], (4) A good performance of redox reaction, containing reduction and oxidation, and (5) Stability and good regenerable ability.

2. Materials and Method

2.1 Material synthesis

The (LSCF3773) powder was prepared by Pechini method (EDTA-citrate complexing) modified by adding ethylene glycol as polymerization agent in order to promote the polymerization with the chelating agent (Ethylenediaminetetra acetic acid, EDTA and Critic acid) [16-18]. To prepare LSCF powder, Firstly, The corresponding metal nitrate precursors; lanthanum (III) nitrate [$La(NO_3)_3$. $9H_2O$, (Himedia)], strontium nitrate [$Sr(NO_3)_2$, (Himedia)], cobalt (II) nitrate hexahydrate [$Co(NO_3)_2.6H_2O$, (Carlo erba)], and iron (III) nitrate nonahydrate [$Fe(NO_3)_3.9H_2O$, (Ajax Finechem)] were mixed and dissolved in 100 ml. of distilled water. Ethylenediaminetetra acetic acid [EDTA, (Ajax Finechem)] as chelating agent was dissolved with Ammonium Hydroxide[NH_4OH 28-30%w/w, (J.T.Baker)] diluted by distilled water. Adding EDTA-NH_4OH solution into the precursor nitrate solution by slowly dropping with Syringe pump (LongerPump) together with continuously stirring. After mixing well between the EDTA-NH_4OH solution and the precursor nitrate solution, Citric acid solution (CA) [Citric acid (monohydrate) 99.5-102%, (Lobachemie)] and ethylene glycol (EG) [Ethanediol, (Ajax Finechem)] was added in this mixed solution respectively. The suitable mole ratio for metal nitrates: EDTA: CA: EG is 1: 1:1.5:1 adapted by [16-17]. Finally, NH_4OH was further added in order to adjust the pH of solution around 6-7, and then the mixed solution was evaporated at temperature of 80-90°C under stirring with sustained pH around 6-7 during the evaporation process until the solution became to be a transparent dark brownish gel. After that, the dark brownish gel was dried in a vacuum oven (Binder) at 120-200°C overnight.

The powder after drying was like a foam and then the powder was ground and then calcined in a tubular furnace in air at 1100°C for 12 h with 2°C/min of heating rate in order to achieve completely the perovskite phase, adapted by [18]. Figure 1 shows the diagram of LSCF powder preparation.

2.2 Characterization

Crystalline phase and crystallite size of the synthesized $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ (LSCF3773) were analyzed by X-ray Diffractometer (Bruker AXS, Diffraktometer D8, 230 V 50Hz 6,5kVA, Germany) using CuKα radiation, λ=1.5418 Å in a range of 20°< 2θ < 80°. Scherrer's equation was used to determine the crystallite size as shown in Equation (1)

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta} \qquad (1)$$

Where D is the average crystallite size (nm), λ is the X-ray wavelength in nanometer (1.5418 A° for CuKα radiation), $\beta_{1/2}$ is the peak width of the diffraction peak profile at half maximum height at any planes in the radiation used and θ is the Bragg diffraction angle at peak position (degrees or radians**)** [22].

2.3 Temperature-programmed reduction technique (CH_4-TPR)

Temperature-programmed reduction of methane technique (CH_4-TPR) was carried out to investigate the performance of reduction with CH_4 on the catalyst's surface in order to determine the suitable temperature for CH_4 partial oxidation, where the oxygen source is only the oxygen lattice of the LSCF as shown in Equation (2) [23-24].

$$LSCFO_y + CH_{4(g)} \rightarrow LSCFO_{y-1} + 2H_{2(g)} + CO_{(g)} \qquad (2)$$

1.0 g. of the sieved catalyst (75-180 μm) was packed into the reactor having 1 cm. of bed height and pretreated in 10 % O_2/Ar to eliminate any possible impurities and to have the oxygen vacancies filled in. 5 %CH_4/Ar was fed at a total flow rate of 200 ml.min^{-1} into the reactor. The temperature was raised up from ambient to 1000°C at 5°C/min. The gaseous outlet stream, contained CH_4, CO_2, CO, H_2, O_2 and Ar, was real-time analyzed by the online MS-Gas analyzer (PFEIFFER, GSD 320 O1, OmniStar Gas analysis system 1-100 amu, 100-230 V, 50/60Hz).

2.4 Packed-bed reactor performance test for co-fed of CH_4 and N_2O

2.0 g. of the sieved catalyst was packed in a quartz tubular reactor with an inside diameter of 4 mm. In the reactor, an inlet gas stream, consisted of CH_4, N_2O, and Ar, was fed with total flow rate of 100 $ml.min^{-1}$. Weight hourly space velocity (WHSV) is 3000 $ml.g_{cat}^{-1}.hr^{-1}$. The effects of CH_4/N_2O molar ratio and operating temperature were studied on CH_4 conversion and product's molar ratio (H_2:CO). N_2O flow rate was fixed at 14.2 $ml.min^{-1}$ and adjusted CH_4 flow rate by Trial and error method in order to achieve nearly 100 % CH_4 conversion and H_2:CO molar ratio approximately led to 2. The operating temperature was varied at 750, 800, 850, 900 and 950°C. The product gas stream was analyzed with an on-line gas chromatography (GC) with thermal conductivity detector and flame ionization detector (Shimadzu GC-2014, TCD/FID detector) using a Molecular Sieve 13X and Porapak N, P, Q packed column and Rtx-1 Alumina as capillary column. Ar was used as the carrier gas. Schematic diagram of the experiment in packed-bed reactor is shows in Figure 2.

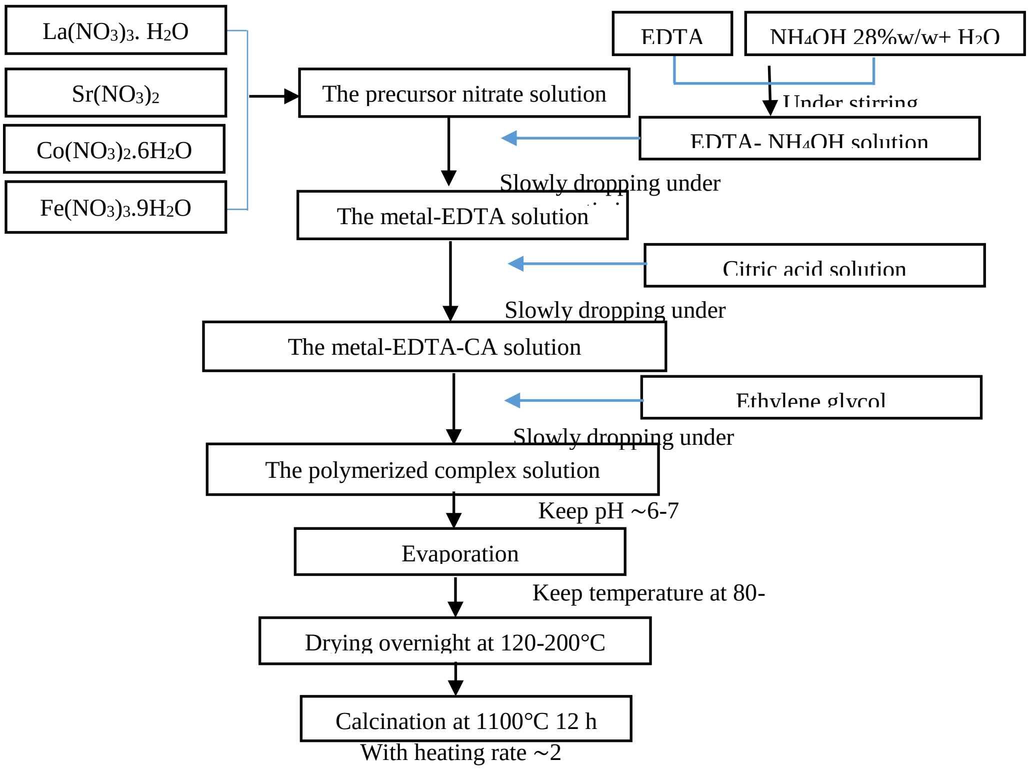


Figure 1. Flow diagram of LSCF preparation by Pechini method (EDTA-citrate complexing) modified by adding ethylene glycol.

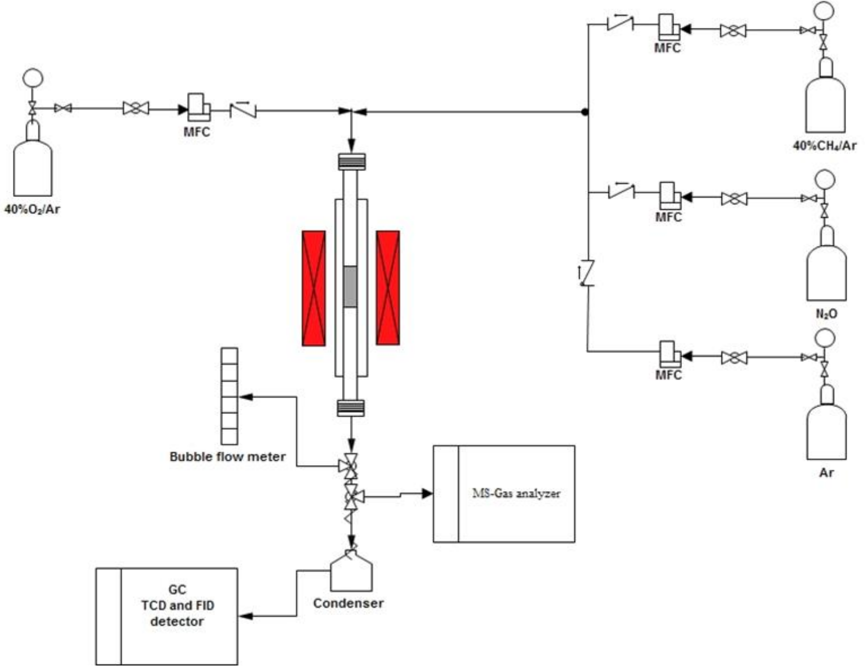
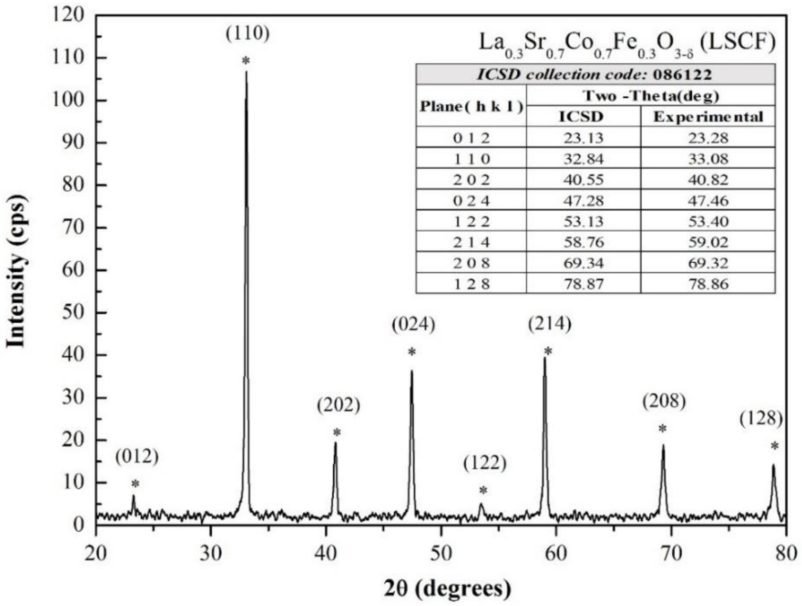


Figure 2. Schematic diagram of CH_4-TPR and CH_4 partial oxidation performance using N_2O.



ICSD collection code: 086122		
Plane(h k l)	Two -Theta(deg)	
	ICSD	Experimental
0 1 2	23.13	23.28
1 1 0	32.84	33.08
2 0 2	40.55	40.82
0 2 4	47.28	47.46
1 2 2	53.13	53.40
2 1 4	58.76	59.02
2 0 8	69.34	69.32
1 2 8	78.87	78.86

Figure 3. The XRD pattern of (LSCF3773) as a single perovskite phase.

In Co-fed N_2O and CH_4 system, at high temperature, Firstly, N_2O was decomposed to be N_2 and O_2 as product. According to the literature review [5, 24-25], possible mechanism of N_2O decomposition on the surface of perovskite catalyst shows By Langmuir-Henshelwood mechanism

$$N_2O_{(g)} + *_{(S)} \rightarrow N_{2(g)} + O^*_{(ads)} \quad (3)$$

$$2O^*_{(ads)} \leftrightarrow O_{2(g)} + 2^*_{(s)} \quad (4)$$

Eley-redeal mechanism

$$N_2O_{(g)} + O*_{(ads)} \rightarrow N_{2(g)} + O_{2(g)} + *_{(s)} \quad (5)$$

Where * is oxygen vacancy or called as active side, O* is an adsorbed oxygen atom.

Generally, for N_2O decomposition over perovskite material as catalyst, Firstly N_2O is adsorbed at oxygen vacancy or active side on LSCF surface and decomposed as N_2 and O* presented in Equation (3). Then, O* atom can bond together with another nearby O* atom absorbed on the surface and generated O_2 molecules. O_2 molecules will be decomposed, dependent on obtained energy and property of catalyst, and when O_2 desorbed on the surface, it presented two oxygen vacancy (2*) as shown in Equation (4). Moreover, N_2O can absorb with non-stable of absorbed oxygen which can bond with O-N in N_2O and then generate N_2, O_2 and vacancy side (*) as can be seen in Equation (5) [5, 26-27].

The efficiency of N_2O decomposition can be calculated from equation (6) [26].

$$N_2O\,\text{decomposition}\,(\%) = \left(\frac{F_{N_2O,in} - F_{N_2O,out}}{F_{N_2O,in}}\right) \times 100 \quad (6)$$

In methane partial oxidation reaction, there are four possible reactions of CH_4 conversion as follows [28]. However, in this study, it expected to achieve as Equation (7), presenting methane partial oxidation reaction and giving 2 of H_2/CO ratio.

$$CH_{4\,(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} + 2H_{2(g)} \quad (7)$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2\,O_{(aq)} \quad (8)$$

$$CH_{4(g)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{(g)} + 2H_2\,O_{(aq)} \quad (9)$$

$$CH_{4(g)} + O_{2(g)} \rightarrow CO_{2(g)} + 2H_{2(g)} \quad (10)$$

The efficiency of methane partial oxidation as Equation (7-10) can be presented by CH_4 conversion, H_2/CO molar ratio and percent concentration of produced gas. The calculation of CH_4 conversion, H_2/CO molar ratio, and percent concentration of produced gas can be determined as follows Equation (11) and (12) respectively.

$$CH_4\,\text{conversion}\,(\%) = \left(\frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}}\right) \times 100 \quad (11)$$

$$H_2\,/\,CO\,\text{molar ratio} = \frac{\text{Moles of } H_2}{\text{Moles of CO}}\ \text{or}\ \frac{F_{H_2}}{F_{CO}} \quad (12)$$

3. Results and Discussion

3.1 Characterization (XRD result)

Crystalline phase of the LSCF3773 powder was shown by XRD pattern following in Figure 3. The XRD pattern presenting the diffraction peaks were 23.28 ° (012), 33.08 ° (110), 40.82 ° (202), 47.40 ° (024), 53.40 ° (122), 59.02 ° (214), 69.32 ° (208), and 78.86 ° (128), which are corresponding to JCSD collection code 086122. And, according to literature of Babiniec et al., LSCF3773 was assigned to cubic phase, which was due to low of La content. [19]. The crystalline phase also mostly achieved a single perovskite phase because there are not other peaks appeared in the pattern. Moreover, From the XRD result, the crystalline size of LSCF3773 (calcined at 1100°C) was 43.24 nm, determined by Scherrer's equation as shown in Equation (1).

3.2 Temperature-programmed reduction of methane (CH4-TPR)

CH_4-TPR profile of LSCF3773 in Figure 4 performs the relationship among an outlet gas stream [$mol.min^{-1}.g^{-1}$] of each gas, Time (min) and Temperature (°C). There are four regions differently in term of reaction pathways at different temperatures. According to Figure 4, at temperature below 500°C, in region I, no reaction occurred on the catalyst surface because at the low temperature, it have no enough energy to overcome activation energy (Ea) of any reactions. For the region II, at temperature in range of 450-800°C, the CH_4-TPR profile presented that CH_4 were slightly consumed, while CO_2 were found in the system. It can be explained that at the moderate temperature, CH_4 can react with oxygen (O*) adsorbed on the catalyst surface or oxygen molecule (O_2) desorbed from the catalyst surface and get CO_2 and H_2O as the products of combustion reaction as shown in Equation (10).

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(aq)} \qquad (10)$$

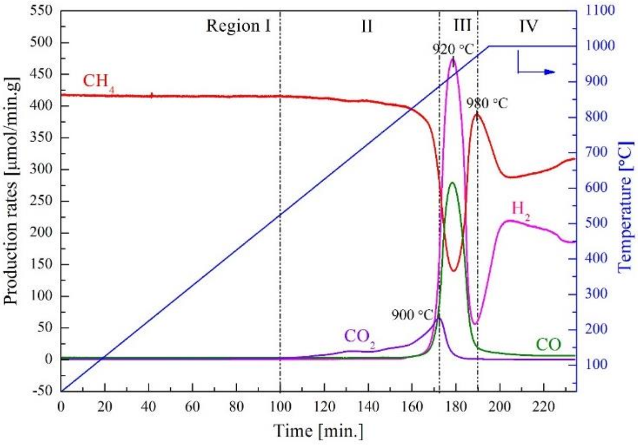


Figure 4. CH_4-TPR profile of $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ (LSCF3773) (The transient temperature program of 25°C-1000°C).

In the region III, at high temperature 900-950°C, an enough high energy can take oxygen away from oxygen lattice of LSCF3773 and then, oxygen atoms can be delivered by other oxygen vacancies as known as diffusion process in the lattice of catalyst. As a result, CH_4 fed as reactant reacted with this oxygen atom at active side and generated H_2 and CO as the main products or known as "Synthesis gas", following the reaction shown in Equation (7).

$$CH_{4\,(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} + 2H_{2(g)} \qquad (7)$$

Moreover, this region presented the consumption peak of CH_4 at the lowest point, which means that at this point, at 920°C, CH_4 was known as "the reducing agent", showing the best of oxidizing with oxygen. It presented the highest peak of products (H_2 and CO) and gave the lowest amount of CO_2. Additionally, In a range of temperature at 900-950°C, an area of the peak can be determined as the amount of methane consumption that are 4422 [mol.min^{-1}.g^{-1}] corresponding to 2211[mol.min^{-1}.g^{-1}] of oxygen storage in lattice (O*) used for this partial oxidation of methane. Regarding to a theory, the maximum of oxygen storage in LSCF3773, which contain maximum 0.4 of oxygen non-stoichiometry (δ) [20].

However, at high temperature 1000°C (Region IV), after CH_4 completely oxidized with oxygen and no oxygen remained in lattice. CH_4 can be decomposed by itself, which generated a carbon deposition (coke) on the quartz tube and also on the surface of catalyst.

Thus, according to the study of CH_4-TPR profile, the result indicated the best temperature of CH_4 partial oxidation reaction with oxygen that is 900-950°C (Region III).

3.3 CH_4 partial oxidation using N_2O as an oxidant

In packed-bed reactor performance test, this work attentively studied (a) the effect of CH_4/N_2O molar ratio on CH_4 conversion and a H_2/CO molar ratio; (b) the effect of operating temperature on CH_4 conversion, and H_2:CO molar ratio. WSHV of the reaction test (100ml.min^{-1}. / 2g of catalyst) is 3000 ml.g^{-1}.hr^{-1}.

(a) Effect of CH_4/N_2O molar ratio on CH_4 conversion and H_2/CO molar ratio

CH_4/N_2O molar ratio was studied by fixing N_2O at 14.2 ml.min^{-1} and adjusting CH_4 with trial and error method depending on the result. The temperature operation was constant at 900°C. As shown in Table 1 and Figure 6, they show an effect on CH_4 conversion and the H_2/CO molar ratio of CH_4/N_2O as feed condition. According to the result, at feed condition CH_4/N_2O as 1:1, reaction condition of reactant (CH_4/O_2) is equal to 2:1 following stoichiometric ratio as theoretical reaction shown in Equation (7). It performed 94.87% CH_4 conversion and 1.89 of H_2/CO molar ratio.

Furthermore, according to the result, an increase of CH_4 flow rate or an increase of CH_4/N_2O molar ratio from 1 to 1.08, 1.75, CH_4 conversion continuously increased from 94.87% to 96.32% and 96.43%, respectively. In contrast, when decreasing CH_4 or decreasing CH_4/N_2O, CH_4 conversion significantly decreased from 94.87% to 77%. Moreover, the increasing of CH_4/N_2O molar ratio made H_2/CO molar ratio nearly approach to 2. The H_2/CO molar ratio also increased from 1.73 to 1.89, 1.99 and 2.19, respectively.

$$CH_{4(g)} + O_{2(g)} \rightarrow CO_{2(g)} + 2H_{2(g)} \qquad (10)$$

(b) Effect of Operating Temperature on CH_4 conversion and H_2/CO molar ratio

According to the study of CH_4/N_2O molar ratio, the suitable feed condition ratio that provided high CH_4 conversion and H_2/CO molar ratio approaching to 2 was 1.08 of CH_4/N_2O molar ratio. Thus, for studying the effect of operating temperature on CH_4 conversion, H_2/CO molar ratio, and the percent concentration of produced gas, the operating temperature were varied from 800°C to 950°C with 5 ºC.min^{-1} in heating rate at the same feed condition ratio CH_4/N_2O as 1.08. The experimental results were reported from Figure 5.

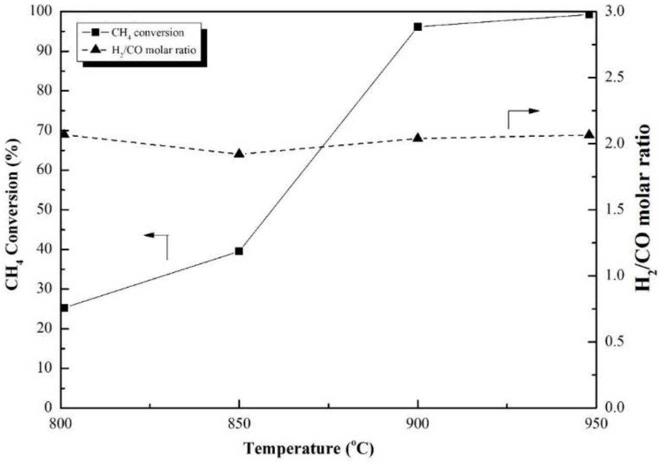


Figure 5. The effect of operating temperature on CH_4 conversion, H_2/CO molar ratio, with WHSV = 3000 ml.g^{-1}.h^{-1}.

Table 1. The Effect of different feed conditions (CH_4/N_2O ratio) on CH_4 conversion and H_2/CO molar ratio.

No.	Feed condition			Reaction condition (CH_4/O_2 ratio)	CH_4 conversion	H_2/CO ratio
	N_2O (ml.min^{-1})	CH_4 (ml.min^{-1})	CH_4/N_2O			
1	14.2	10	0.7	1.41	77.00	1.73
2	14.2	14	1	2	94.87	1.89
3	14.2	15.4	1.08	2.17	96.18	2.04
4	14.2	17.5	1.23	2.46	96.43	2.19

However, when continuously increasing CH_4 contents until 1.75 of CH_4/N_2O molar ratio, the partial oxidation of methane possibility significantly decreased. In the contrast, it made the possibility of side reaction as Equation 10 [28,], which In this case, it can be explained as 2 possible assumptions that are i.) at the same temperature, excess of CH_4 contents in feed stream can unbalance for the reduction reaction of CH_4 with O* on the surface or in the lattice of LSCF3773. Consequently, CH_4 has a chance to react with oxygen molecule and generate CO_2 and 2 moles of H_2 as product. This assumption can correspond to presenting of H_2/CO more than 2 and also appearing of CO_2 in the system. ii) CH_4 may be decomposed by itself and generate carbon coke on the catalyst's surface.

According to the result as shown in the Figure 5, CH_4 conversion was increased with increasing temperature. At initial temperature at 800 °C, CH_4 conversion achieved only 30%. When temperature are increased from 800°C to 850°C, 900°C , and 950°C, CH_4 conversion increasingly achieved from 25.27% to 39.56%, 96.18%, and 99.28%, respectively. Moreover, increasing with temperature made the product as H_2/CO molar ratio differ from at different temperatures. H_2/CO molar ratios were changed from 2.07 to 1.92, 2.04, and 2.06 at 800°C 850°C 900°C and 950°C, respectively. As shown in the result, CH_4 conversion increased with increasing with temperature. The behavior of studying the effect operating temperature on CH_4 conversion corresponded with reaction kinetic. Normally, the reaction rate will be increased with increasing temperature as the Theory of Arrhenius law ($k = Ae^{-Ea/RT}$).

As the result, the best performance took place at 950°C with 99.28% CH_4 conversion and 2.06 of H_2/CO molar ratio.

3.4 Stability Test

According to the performance study, in co-feed N_2O and CH_4 system, the best operating condition is 14.2 $ml.min^{-1}$ N_2O, 15.4 $ml.min^{-1}$ CH_4, and 70.4 $ml.min^{-1}$ Ar at 950°C in operating temperature. This condition was used in the stability test. The continuous flow reaction run for 10 hours as shown the result with CH_4 conversion (%) and H_2/CO molar ratio in Figure 6. After that, this material will be analyzed by XRD technique as shown in Figure 7.

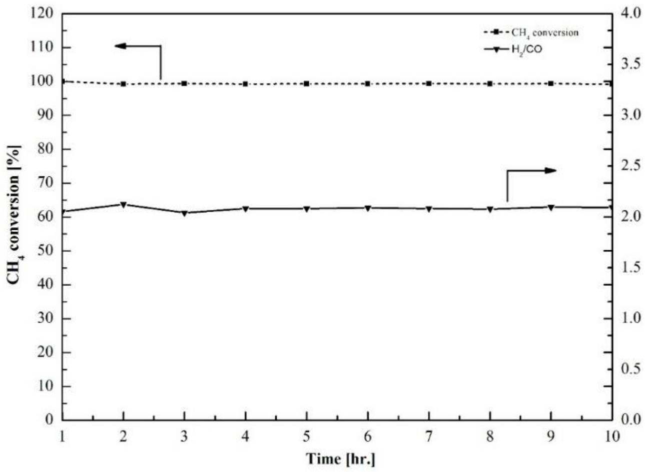


Figure 6. The relationship between CH_4 conversion and H_2:CO ratio with time.

The stability result of synthesis gas production over perovskite LSCF3773 via using N_2O as an oxygen source was shown in Figure 6. CH_4 conversion achieved and maintained with 99% along 10 hours of continuous reaction. This result displayed that the pervoskite can be used by continuously redox reaction, oxidation and reduction, until 10 hours with stable activity. Moreover, the products of reaction as well as presented 2 of H_2/CO molar ratio, which means the dominant reaction still to perform as partial oxidation creating syngas products. The co-feed N_2O and CH_4 reaction contains two main reactions follow:

In generation step: CH_4 is oxidized with oxygen (O*) both on the surface and in the lattice of LSCF3773, thus oxygen (O*) got away from LSCF3773 as shown as Equation (13).

$$La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_3 + CH_4 \rightarrow La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta} + 2H_2 + CO \qquad (13)$$

Meanwhile, N_2O simultaneously decomposed on the surface of LSCF3773 and provided O* into oxygen vacancy (active site), as the result, LSCF3773 was replenished by oxygen as shown in the re-oxidation Equation (14)

In re-generation step: O* from N_2O decomposition is re-oxidized to recover the oxygen vacancy.

$$La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta} + O^{*} \rightarrow La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_3 \qquad (14)$$

As above mention, Consequently, Co-feed N_2O and CH_4 can continuously run over LSCF3773 with stable activity performance, this support the perovskite material have an regenerable ability. The XRD shown in Figure 7.is an evident for regeneration of perovskite by total O_2 treatment.

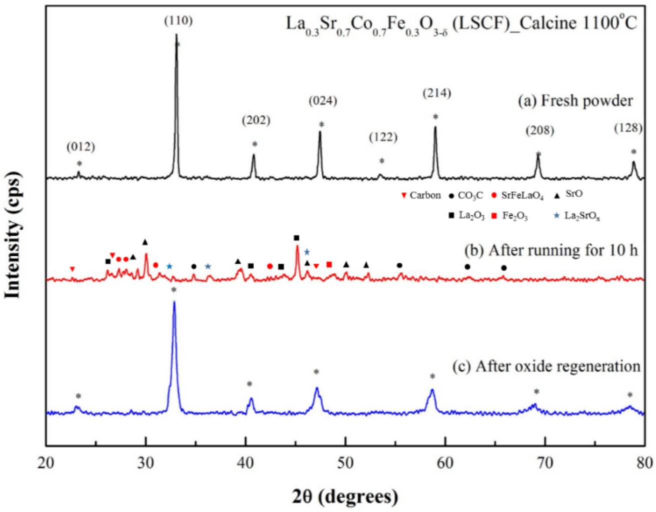


Figure 7. XRD patterns of LSCF (a) Fresh powder, (b) After running, (c) After oxide regeneration

From The Figure 7, after running for 10 hours of LSCF3773, the XRD result shows the characteristic peaks of CO_3C, La_2O_3, $SrFeLaO_4$, Fe_2O_3, SrO, La_2SrO_x, and some carbon depositions (Figure 7(b).). This result can assumed that both O* on the surface and in the lattice got away from LSCF3773 structure, as the result, the perovskite phase disappeared and cannot detected by XRD. However, after taking O_2 until assure that O_2 was replenished in full of the lattice. The Figure 7(c) displays that the perovskite phase appear again in the structure. Therefore, this LSCF3773 can be used in the new reaction later. In comparison with other catalyst materials such as Ni, other metals, the perovkite has an outstanding in terms of stable activity and generable property [24, 29-30]. However, the limitation and maximum regeneration times of the perovkite materials depend on the different composition. For example, according to previous study [29], $La_{0.8}Sr_{0.2}Co_{0.9}Fe_{0.1}O_3$ was used in methane partial oxidation with absence of O2 in system with higher 96% CH_4 conversion for 29th cycle, but at up to 15th cycle, CO selectivity decrease 95 to 36% and oxygen storage capacity decrease from 89.4 to 35 $\mu mol/g_{cat}$, which may cause by carbon decomposition and the perovskite structure perhaps tend to permanent loss of the perovkite phase respectively. In contrast, $La_{0.8}Sr_{0.2}FeO_3$ presented about 80% CH4 conversion for 29th cycle, but CO selectivity and oxygen storage capacity remain stable at 97% and 73 $\mu mol/g_{cat}$ respectively. Thus, the selection of perovskite type materials rely on each objectives. In this study, $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ can meet the objectives in terms of high CH_4 conversion, selective with 2 of H_2/CO ratio, and ability for continuous running for 10 hours.

4. Conclusion

Perovskite material $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_{3-\delta}$ (LSCF3773) was prepared by Pechini method (EDTA-citrate complexing method) modified by adding ethylene glycol and was calcined at 1100°C for 12 hr. to perform as perovskite phase. LSCF3773 presented pure perovskite phase shown in XRD pattern and gave 43.24 nm in crystalline size. From the result, at the feed condition CH_4/N_2O molar ratio as 1.08 and at 950°C in operating temperature, the study report was found that the best performance of CH_4 conversion can achieve 99.28%molar ratio and perform 2.06 as H_2/CO molar ratio. Moreover, in the stability test, LSCF3773 can perform continuously with 99% CH_4 conversion throughout 10 hours and also gave approaching to 2 of H_2/CO molar ratio approximately. Although, LSCF3773 phase after the reaction was detected with a complicated phase and found with a disappearance of LSCF phase, it can be regenerated by full filling with O_2 into the lattice of structure in order to appear a single LSCF perovskite phase again.

For experimental results in this work, LSCF3773 was considered as 1.) A catalyst because it can help for continuous reaction with oxygen vacancy and oxygen mobility property of pervoskite, and also act as 2.) A reactant (O* source in lattice), as confirmed in CH_4-TPR, in the synthesis gas production via integrating N_2O decomposition with methane partial oxidation. Moreover, this work indicated LSCF3773 as regenerable phase property by replenishment of O_2. This is one of the strong points for the perovskite material, which can regenerate catalyst for long continuous running and reuse catalyst powder in the reaction again.

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