Effects of Mg, Ca, Sr, and Ba Dopants on the Performance of La$_2$O$_3$ Catalysts for the Oxidative Coupling of Methane

Danusorn Kiatsaengthong, Kanticha Jaroenpanon, Pooripong Somchuea, Thanaphat Chukeaw, Metta Chareonpanich, Kajornsak Faungnakwajik, Hiesang Sohn, Günther Rupprechter, and Anusorn Seubsai

ABSTRACT: Oxidative coupling of methane (OCM) is a reaction to directly convert methane into high value-added hydrocarbons (C$_2$+) such as ethylene and ethane using molecular oxygen and a catalyst. This work investigated lanthanum oxide catalysts for OCM, which were promoted with alkaline-earth metal oxides (Mg, Ca, Sr, and Ba) and prepared by the solution-mixing method. The synthesized catalysts were characterized using X-ray powder diffraction, CO$_2$-programmed desorption, and X-ray photoelectron spectroscopy. The comparative performance of each promoter showed that promising lanthanum-loaded alkaline-earth metal oxide catalysts were La-Sr and La-Ba. In contrast, the combination of La with Ca or Mg did not lead to a clear improvement of C$_2$+ yield. The most promising LaSr50 catalyst exhibited the highest C$_2$+ yield of 17.2%, with a 56.0% C$_2$+ selectivity and a 30.9% CH$_4$ conversion. Catalyst characterization indicated that their activity was strongly associated with moderate basic sites and surface-adsorbed oxygen species of O$_2^-$. Moreover, the catalyst was stable over 25 h at a reactor temperature of 700 °C.

1. INTRODUCTION

Methane (CH$_4$) is a chemical compound abundantly available in nature, which is mainly created from cultivation activities, livestock farming, mining combustion, and human/industrial waste. Methane can be used in industrial chemical processes and as fuel for ovens, homes, water heaters, kilns, automobiles, and turbines. Being the main component of natural gas, methane is important for electricity generation through combustion in gas turbines or steam generators. Moreover, it can be used to produce hydrogen gas via steam reforming of methane. In 2020, methane was used to produce over 52 million metric tons of hydrogen, which was used in petroleum refineries, chemical productions, and food industries. Moreover, there are several studies on using methane as a reactant to produce value-added chemicals via different methods. One of the prevalent reactions is the oxidative coupling of methane (OCM) over a suitable heterogeneous catalyst.

OCM, discovered by Keller and Bhasin in 1982, is a reaction to convert methane into high value-added hydrocarbons such as ethylene, ethane, propylene, and propane (denoted as C$_2$+). However, byproducts such as carbon monoxide (CO) and carbon dioxide (CO$_2$) are also produced. The proposed dominant mechanism involves dehydrogenation through methane activation by adsorbed oxygen species on the catalyst surface, forming methyl radicals. The coupling of two methyl radicals subsequently occurs to generate ethene molecules that can be dehydrogenated to ethylene. During the reaction, water may be formed as a byproduct. CO and

Received: August 30, 2021
Accepted: December 22, 2021
Published: January 4, 2022
CO₂ can also originate from the nonselective oxidation of hydrocarbons. Several catalysts have been investigated in OCM, including rare earth oxide catalysts, which exhibited good activity due to the presence of reactive oxygen sites produced by surface oxygen vacancies. The reported catalysts provided C²⁺ yields >25% with 48–90% C₂⁺ selectivities and 33–68% CH₄ conversions at temperatures between 677 and 927 °C, which was still inefficient. This is due to the homogeneous gas-phase processes mainly controlling the coupling reaction. Therefore, at very high temperatures, the hydrocarbon yield is limited, regardless of the number of surface catalytic sites and methyl radicals. For this reason, highly efficient OCM catalysts should not only initiate the formation of free CH₃ radicals at lower temperatures but also inhibit the nonselective oxidation of methane and hydrocarbons to CO₂. Preventing COx formation is, therefore, the major challenge of OCM.

Among OCM catalysts, lanthanum-based catalysts are of great interest that have also been modified with different promoters. In general, the addition of a catalyst promoter may improve specific properties, such as reducing the reaction temperature, increasing thermal stability, increasing basic sites or base strength, and modifying the mobility of lattice oxygen. Lanthanum oxides catalysts were first modified with alkaline by DeBoy and Hicks, who reported that 1 wt % alkaline-earth metal oxide could enhance the selectivity of lanthanum oxide catalysts: a La-Li catalyst had the highest C₂⁺ selectivity of 75.9% with a 21.6% CH₄ conversion. Song et al. reported that Sr-promoted La performed well at low temperatures (<500 °C) with excellent thermal stability. Jiang et al. reported that at lower temperatures, unpromoted lanthanide oxide nanorods outperformed lanthanum oxide nanopowders, nanosheets, and nanoflowers. Their best result was 14.8% C₂⁺ yield with a 45.9% C₂⁺ selectivity and a 32.3% CH₄ conversion. Alkaline-earth metal oxide-promoted lanthanum oxide catalysts were also prepared without support. Uphade et al. and Choudhary et al. showed that unsupported lanthanum-promoted catalysts exhibited higher C₂⁺ yields than those with supports.

According to these reports, the basicity of the catalysts strongly influenced catalytic OCM activity. The addition of alkaline-earth metal oxides was reported to increase the basic sites and base strengths of catalysts, leading to an increase in C₂⁺ formation. For example, Lim et al. used CaTiO₃, SrTiO₃, and BaTiO₃ perovskite catalysts in OCM and found that SrO supported on BaTiO₃ produced the highest C₂⁺ yield (17.6% at a reaction temperature of 725 °C), resulting from strong surface basicity. Elkins et al. investigated different alkali and alkaline-earth metals (Li, Na, Mg, and Ca)-doped rare earth oxide (Sm₂O₃, TbO₂, PrOₓ, and CeO₂) catalysts supported on nanoparticle magnesium oxide (n-MgO) for OCM. They found that Li-TbOₓ supported on n-MgO outperformed all other prepared catalysts because of its stronger basic sites. One strategy to increase C₂⁺ formation is to control the formation of CH₃ radicals via creating surface electrophilic oxygen anions such as O⁻, O₂⁻, O₂²⁻, and O₂⁴⁻, as these species are crucial for C₂⁺ or CO₂ formation. It has been reported that the surface O²⁻ lattice oxygen usually creates CO₂ while O⁻, O₂⁻, and O₂²⁻ species generate C₂⁺ products. Thus, some studies attempted to add alkaline-earth metal to lanthanum

Figure 1. Effects of (a) Mg, (b) Ca, (c) Sr, and (d) Ba loading on La catalysts. Testing conditions: feed gas ratio of CH₄/O₂/N₂ = 3:1:4, total feed flow rate = 35 mL min⁻¹, total weight catalyst = 50 mg, and reactor temperature = 700 °C.
oxide catalysts because alkaline-earth metals usually act as oxygen-to-peroxide activators, which would create peroxide anions subsequently added to vacant sites in the lanthanum oxide lattice.

However, mechanistic details are still lacking and further studies are required, focusing on surface basicity, structural properties, and product optimization, which would be beneficial for future applications. Herein, (unsupported) lanthanum oxide mixed with oxides of alkaline-earth metal, including Mg, Ca, Sr, and Ba, are systematically investigated as OCM catalysts. Furthermore, the characterization of structure and adsorption properties enables us to understand the relationship between surface properties and catalytic performance.

2. RESULTS AND DISCUSSION

2.1. Activity of Lanthanum Oxide Catalysts Loaded with Different Alkaline-Earth Metal Oxides. The kinetic performance of lanthanum oxide catalysts with different loadings (0–60 wt %) of alkaline-earth metal oxide (i.e., Mg, Ca, Sr, or Ba) was evaluated by the OCM reaction under identical conditions, as illustrated in Figure 1. The catalysts are defined as LaZY (where Z is the alkaline-earth metal (Mg, Ca, Sr, or Ba) and Y is its weight percentage on the catalyst). It was found that the lanthanum oxide catalyst exhibited a 12.7% C₂+ yield with a 48.8% C₂+ selectivity and a 26.1% CH₄ conversion, while the pure oxides of Mg, Ca, Sr, or Ba had a lower C₂+. The most promising alkaline-earth metal oxide-promoted lanthanum oxide catalysts were La-Sr and La-Ba, whereas La-Ca or La-Mg did not significantly improve the C₂+ yield. The highest C₂+ yield was observed for LaSr50, giving a C₂+ yield of 17.2% with a 56.0% C₂+ selectivity and a 30.9% CH₄ conversion. The most active catalyst in the groups of Mg, Ca, and Ba was LaMg10 (15.0% C₂+ yield), LaCa30 (15.4% C₂+ yield), and LaBa50 (15.9% C₂+ yield), respectively. Comparing the highest C₂+ yields in each group, the catalysts were ranked as follows: LaSr50 > LaBa50 > LaCa30 > LaMg10.

The most active catalysts in the groups were further evaluated for OCM performance at different reactor temperatures (450–800 °C), as shown in Figure 2. All four catalysts were activated at approximately 500–550 °C; then, the performance of all four catalysts sharply increased to their maximum values at 700–750 °C. Interestingly, at 650 °C, LaSr50 exhibited much higher CH₄ conversion and C₂+ yield compared to the other three catalysts and kept exhibiting high performance until 750 °C, indicating that LaSr50 is superior to the other catalysts, especially in the reactor temperature range of 650–750 °C. At high reactor temperatures (750–800 °C), the C₂+ selectivities of the catalysts dramatically decreased with a relatively small change of CH₄ conversion, leading to a gradual decrease in the overall performance (i.e., C₂+ yield).
This could be because of the partial combustion of the products at high temperatures.  

2.2. Catalyst Characterization.  

2.2.1. XRD Analysis.  
Based on the activity study in Section 2.1, the optimal lanthanum oxide catalysts from each group of alkaline-earth metal loading were LaSr50, LaBa50, LaCa30, and LaMg10. The crystal structures of the best lanthanum oxide catalysts were examined by X-ray diffraction (XRD), as depicted in Figure 3. Details on the diffraction peaks are collected in Table S1. XRD peaks of La2O3 were observed for all catalysts. Moreover, XRD peaks of La(OH)3 were observed in LaMg10 and LaCa30 catalysts, which probably resulted from the interaction of La2O3 with moisture after calcination. XRD peaks indicating the presence of MgO, CaO, SrO, or BaO were observed for LaMg10, LaCa30, LaSr50, and LaBa50, respectively. SrCO3 and BaO2 were also detected but in small amounts. Nevertheless, the La2O3 phase interacting with the specific alkaline-earth metal oxide was considered as an active phase in the reaction. Interestingly, upon modification with alkaline-earth metal oxide, the crystallite size of La2O3 became smaller (see the crystallite size of La2O3 of each catalyst in Table S1), paralleled by an increase of C2+ yield. The crystallite sizes of La2O3 were: LaSr50 (21.9 nm) < LaBa50 (36.6 nm) < LaCa30 (37.0 nm) < LaMg10 (46.0 nm), inverse to the orders of C2+ yield. Note that the XRD patterns of the spent catalysts (after being used for 25 h) were also collected (Figure S1). It was observed that all of the XRD peaks of each spent catalyst did not considerably change compared to those of its fresh catalyst (Figure 3).

2.2.2. N2 Sorption Analysis. The Brunauer–Emmett–Teller (BET) surface areas of both the pure fresh La and Sr catalysts and the fresh and spent bimetallic catalysts were evaluated using the nitrogen sorption–desorption technique (Table 1). The BET surface area of LaSr50 was 4.3 m² g⁻¹ compared to 2.3 m² g⁻¹ for the La catalyst and 0.4 m² g⁻¹ for the Sr catalyst. This correlates well with the XRD results (Figure 3) since smaller crystalline size occurs in the catalysts with larger surface areas. This could be because the second component (i.e., Sr) prevents the crystal growth of La2O3. LaMg10 showed a smaller BET surface area relative to the fresh one, which could be because of the aggregation of the catalyst particles. Note that the pore volume and pore size of all of the samples appeared to be undetectable because no hysteresis loops, i.e., nonporous materials, were found.

2.2.3. CO2-TPD Analysis. The characterization of the optimal catalysts, including LaMg10, LaCa30, LaSr50, and LaBa50, was performed using CO2-TPD, as shown in Figure 4. This technique provides information on the nature of the surface basic sites of the catalysts. In CO2-TPD, CO2 desorption was measured in a temperature range of 50–900 °C. Generally, a peak that appears at the highest temperature indicates the highest base strength of the surface. In the CO2-TPD profiles, peaks were assigned to three temperature regions: below 200, 200–600, and above 600 °C, denoted as weak, moderate, and strong surface alkaline sites, respectively. It is widely known that moderate surface alkaline sites are crucial in improving C2+ selectivity. These active sites are generally inactive at low temperatures due to CO2 adsorption. As the reaction temperature increases, the CO2 molecules desorb and then the active sites are available to activate the CH4 molecules. For strong surface alkaline sites, they easily capture CO2 and convert it to stable carbonates that are inactive in the OCM reaction. Thus, it is reasonable to assume that the moderate surface alkaline sites play a crucial role in the OCM reaction. As illustrated in Figure 4 and by the relative peak areas in Table S2, the amount of the moderate surface alkaline sites play a crucial role in the OCM reaction. As illustrated in Figure 4 and by the relative peak areas in Table S2, the amount of the moderate surface alkaline sites play a crucial role in the OCM reaction.

Table 1. BET Surface Area of the Fresh and Spent LaZY Catalysts

| catalyst | fresh | spent |
|----------|-------|-------|
| La       | 2.3   | n/a   |
| Sr       | 0.4   | n/a   |
| LaSr50   | 4.3   | 4.1   |
| LaMg10   | 18.6  | 2.5   |
| LaCa30   | 3.0   | 2.9   |
| LaBa50   | 0.2   | 0.2   |

Figure 3. XRD patterns of fresh LaMg10, LaCa30, LaSr50, and LaBa50.

Figure 4. CO2-TPD profiles of LaMg10, LaCa30, LaSr50, and LaBa50.

This could be because of the partial combustion of the products at high temperatures.  

2.2. Catalyst Characterization.  

Based on the activity study in Section 2.1, the optimal lanthanum oxide catalysts from each group of alkaline-earth metal loading were LaSr50, LaBa50, LaCa30, and LaMg10. The crystal structures of the best lanthanum oxide catalysts were examined by X-ray diffraction (XRD), as depicted in Figure 3. Details on the diffraction peaks are collected in Table S1. XRD peaks of La2O3 were observed for all catalysts. Moreover, XRD peaks of La(OH)3 were observed in LaMg10 and LaCa30 catalysts, which probably resulted from the interaction of La2O3 with moisture after calcination. XRD peaks indicating the presence of MgO, CaO, SrO, or BaO were observed for LaMg10, LaCa30, LaSr50, and LaBa50, respectively. SrCO3 and BaO2 were also detected but in small amounts. Nevertheless, the La2O3 phase interacting with the specific alkaline-earth metal oxide was considered as an active phase in the reaction. Interestingly, upon modification with alkaline-earth metal oxide, the crystallite size of La2O3 became smaller (see the crystallite size of La2O3 of each catalyst in Table S1), paralleled by an increase of C2+ yield. The crystallite sizes of La2O3 were: LaSr50 (21.9 nm) < LaBa50 (36.6 nm) < LaCa30 (37.0 nm) < LaMg10 (46.0 nm), inverse to the orders of C2+ yield. Note that the XRD patterns of the spent catalysts (after being used for 25 h) were also collected (Figure S1). It was observed that all of the XRD peaks of each spent catalyst did not considerably change compared to those of its fresh catalyst (Figure 3).

2.2.2. N2 Sorption Analysis. The Brunauer–Emmett–Teller (BET) surface areas of both the pure fresh La and Sr catalysts and the fresh and spent bimetallic catalysts were evaluated using the nitrogen sorption–desorption technique (Table 1). The BET surface area of LaSr50 was 4.3 m² g⁻¹ compared to 2.3 m² g⁻¹ for the La catalyst and 0.4 m² g⁻¹ for the Sr catalyst. This correlates well with the XRD results (Figure 3) since smaller crystalline size occurs in the catalysts with larger surface areas. This could be because the second component (i.e., Sr) prevents the crystal growth of La2O3. LaMg10 showed a smaller BET surface area relative to the fresh one, which could be because of the aggregation of the catalyst particles. Note that the pore volume and pore size of all of the samples appeared to be undetectable because no hysteresis loops, i.e., nonporous materials, were found.

2.2.3. CO2-TPD Analysis. The characterization of the optimal catalysts, including LaMg10, LaCa30, LaSr50, and LaBa50, was performed using CO2-TPD, as shown in Figure 4.
2.2.4. XPS Analysis. The surface oxygen species of the optimal catalysts were further investigated using X-ray photoelectron spectrometry (XPS), as shown in Figure 5. These surface oxygen species in the O 1s region can be classified as follows: superoxides (O$_2^-$), peroxide ions (O$^-$), hydroxide ions (OH$^-$), carbonates (CO$_3^{2-}$), and lattice oxygens (O$^{2-}$). Among these, the O$_2^-$ species are believed to play a crucial role in the activation of CH$_4$. Thus, the relative amount of each specified oxygen species for each catalyst was determined to identify its correlation with the CH$_4$ conversion, as summarized in Table 2. Note that (i) the CO$_3^{2-}$ species are only present in LaSr$_{50}$ (Figure 5c) as was indicated by the XRD spectra (see Figure 3) and (ii) the binding energies of O$^-$, OH$^-$, and CO$_3^{2-}$ species are very close (approximately 531 eV). These species have been combined into one peak at 531 eV. The quantified XPS peaks of O$_2^-$ in Table 2 show that LaMg$_{10}$ had the highest percentage fraction of O$_2^-$, followed by LaSr$_{50}$, LaCa$_{30}$, and LaBa$_{50}$. These orders are consistent with the orders of CH$_4$ conversion. Thus, the quantified peaks of O$_2^-$ species could be used to describe the performance of each catalyst in terms of activation of CH$_4$.

2.3. Correlation of Catalyst Performance with Catalyst Properties. The C$_2$ selectivity of each catalyst was plotted against the relative quantity of the moderate surface alkaline sites (Figure 6a), and the CH$_4$ conversion of each catalyst was plotted against the percentage fraction of O$_2^-$ (Figure 6b). As observed in Figure 6a, the C$_2$ selectivity appears to improve when the quantity of the moderate surface...
alkaline sites increases, confirming that the moderate surface alkaline sites are essential in promoting the C2+ formation. In Figure 6b, the percentage fraction of O2− also appears to correlate with the CH4 conversion, suggesting that CH4 conversion in the OCM reaction could be improved by designing a catalyst with a relatively high amount of O2−. Together, these plots suggest that a catalyst with a relatively high quantity of moderate surface alkaline sites and a relatively high amount of O2− can be expected to exhibit a high C2+ yield.

2.4. Stability of the LaSr50 Catalyst. To determine the best catalyst, the stability of LaSr50 was tested over 25 h, as shown in Figure 7. The C2+, yield, C2+, selectivity, and CH4 conversion were maintained at approximately 17, 57, and 30%, respectively, throughout the entire period, with hardly any change in selectivity and conversion. This indicates that the catalyst is robust against deactivation.

2.5. Current La-Based Catalysts Compared to Others. Figure 8 shows a review of various La-based catalysts for the OCM reaction that have been reported in the literature, and the details of each catalyst are described in Table S3. To be commercially viable, OCM catalysts should have a CH4 conversion of more than 30% and a C2+ selectivity of more than 80%.31 The catalysts investigated here fall outside of the commercial range. Several catalysts with a CH4 conversion of more than 30% have been observed, but their C2+ selectivity is below 80%. Most of the catalysts were operated in the reaction temperature range of 750−800 °C. Our current LaSr50 performed well at a lower temperature (700 °C), but more progress is required, particularly in increasing the C2+ selectivity to 80% while retaining CH4 conversion. Interestingly, a few reports showed that Li-La-Mg catalysts produced high C2+ selectivity (54−98%) but low CH4 conversion (22−24%) at a reaction temperature range of 650−700 °C.32,33 The goal of work in this area is to increase CH4 conversion rates, while maintaining this excellent C2+ selectivity and mild conditions. Accordingly, further investigation of the La-based catalysts is needed.

3. CONCLUSIONS

Alkaline-earth metal oxide-promoted lanthanum oxide catalysts were synthesized by the solution-mixing method. It is shown that alkaline-earth metal oxides, including MgO, CaO, SrO, and BaO, enhance the catalytic activity of the pure lanthanum oxide catalyst for OCM. The outstanding catalyst was LaSr50, followed by LaBa50, LaCa30, and LaMg10. The highest C2+ yield of 17.2% was obtained for LaSr50, with a 56.0% C2+ selectivity and a 30.9% CH4 conversion. The improvement of catalyst performance for C2+ formation is strongly associated with (i) a reduction of La2O3 crystallite sizes when each alkaline-earth metal oxide is added to the La2O3 catalyst, (ii) the presence of the moderate surface alkaline sites, and (iii) a high amount of O2− species. Furthermore, the stability of LaSr50 was excellent, with no changes over 25 h. In situ studies are planned for the near future to gain further insight under reaction conditions.

4. MATERIAL AND METHODS

4.1. Catalyst Preparation. Lanthanum(III) nitrate hexahydrate [La(NO3)3·6H2O, 99.00%, HiMedia], calcium nitrate [Ca(NO3)2·4H2O, 99.00%, Kemaus], magnesium nitrate hexahydrate [Mg(NO3)2·6H2O, 99.5%, QReC], strontium nitrate [Sr(NO3)2·99.00%, HiMedia], and barium nitrate [Ba(NO3)2·99.00%, HiMedia] were used as precursors for oxides of La, Ca, Mg, and Ba, respectively. The general procedure for preparing metal oxide catalysts is as follows. Each precursor was dissolved in ionized water to obtain the desired metal concentration. Weights of La and X (X = Mg, Ca, Sr, and Ba) were determined, and each metal solution was
pipetted into a beaker to obtain a desired weight percentage of the metal components. The weight percentages of X ranged from 0 to 100 wt % on La. The atomic weight percentages of all of the prepared catalysts are shown in Tables S4−S7. After that, the mixture was stirred at room temperature for 1 h, followed by heating to 115 °C until dry. Then, the dried sample was calcined at 800 °C for 2 h in an air furnace with a heating rate of 5 °C min−1 and subsequently cooled down to room temperature.

4.2. Catalytic Activity Studies. The activity of each catalyst was evaluated in a plug flow reactor at atmospheric pressure, with the reactor temperature ranging from 450 to 800 °C. A sample (50 mg) was sandwiched between layers of quartz wool in a quartz tube reactor (an inner diameter of 0.5 cm with a length of 40 cm). The length of the catalyst bed was approximately 0.5 cm. The feed gas consisted of methane (CH4, 99.999%, Praxair), oxygen (O2, 99.999%, Praxair), and nitrogen (N2, 99.999%, Praxair) at a volume ratio of CH4/O2/N2 = 3:1:4.13 The inlet gas flow rate was 35 mL min−1, corresponding to a gas hourly space velocity (GHSV) of 13 400 h−1. All feed flow rates were controlled using mass flow controllers (Aalborg GFC17). The effluent was analyzed by gas chromatography using a flame ionization detector (FID); for quantifying C2+, including C2H4, C2H6, C3H6, C3H8, C4H8, and C4H10) and a thermal conductivity detector (TCD; for quantifying CO, CO2, and CH4). The activity of each catalyst was evaluated 1 h after the system reached the set point. Each experiment was performed a minimum of three times and plotted as an average value with error bars. Each standard gas was used to make a five-point calibration curve with a coefficient of determination (R2 > 0.99). A time-on-stream experiment over 25 h was conducted to monitor the catalysts’ stability. Equations 1−4 are used for calculating the % CH4 conversion, % C2+ selectivity, % COx selectivity, and % C2+ yield, respectively.

\[
\text{% CH}_4 \text{ conversion} = \left\{ \left[ 2(n_{C_2H_4} + n_{C_2H_6}) + 3(n_{C_3H_8} + n_{C_3H_6}) + 4(n_{C_4H_8} + n_{C_4H_6} + n_{C_4H_10}) \right] + n_{CO} + n_{CO_2} + n_{CH_4} \right\} \times 100
\]

\[
\text{% C}_2+ \text{ selectivity} = \left\{ \left[ 2(n_{C_2H_4} + n_{C_2H_6}) + 3(n_{C_3H_8} + n_{C_3H_6}) + 4(n_{C_4H_8} + n_{C_4H_6} + n_{C_4H_10}) \right] + n_{CO} + n_{CO_2} \right\} \times 100
\]

\[
\text{% COx selectivity} = \left\{ n_{CO} + n_{CO_2} \right\} \times 100
\]

\[
\text{% C}_2+ \text{ yield} = \frac{\text{CH}_4 \text{ conversion} \times \text{% C}_2+ \text{ selectivity}}{100}
\]
detector. The binding energy of each element in the catalysts was analyzed by X-ray photoelectron spectrometry (XPS, Kratos Axis Ultra DLD, using Al Kα radiation).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04738.

XRD patterns of spent catalysts; details of crystalline phases; relative number of CO₂-TPD peaks; lanthanum-containing catalysts reported in the literature; and percentages by weight and atomic mass of catalysts (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

Anusorn Seubsai — Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand; Center of Excellence on Petrochemical and Materials Technology and Research Network of NANOTEC—KU on NanoCatalysts and NanoMaterials for Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand; orcid.org/0000-0001-8336-6590; Email: fengasn@ku.ac.th

**Authors**

Danusorn Kiatsaengthong — Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

Kanticha Jaroenpanon — Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

Pooripong Somchuea — Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

Thanaphat Chukeaw — Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand; Center of Excellence on Petrochemical and Materials Technology, Kasetsart University, Bangkok 10900, Thailand

Metta Chareonpanich — Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand; Center of Excellence on Petrochemical and Materials Technology and Research Network of NANOTEC—KU on NanoCatalysts and NanoMaterials for Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand; orcid.org/0000-0002-4333-337X

Kajornsak Faungnawakij — National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency, Khlong Luang, Pathum Thani 12120, Thailand; orcid.org/0000-0002-4724-0613

Hiesang Sohn — Department of Chemical Engineering, Kwangwoon University, Seoul 01897, Korea; orcid.org/0000-0002-4164-9397

 Günther Ruppprecht — Institute of Materials Chemistry, TU Wien, Vienna 1060, Austria; orcid.org/0000-0002-8040-1677

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.1c04738

### ACKNOWLEDGMENTS

This research work was funded by the National Research Council of Thailand (NRCT): NRCT5-R6A63002-11; the Fundamental Fund, Thailand: FF(KU)21.65; the Kasettsart University Research and Development Institute (KURDI), Thailand; the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand; and the Center of Excellence on Petrochemical and Materials Technology, Thailand. G.R. acknowledges support by the Austrian Science Fund (FWF) via SFB TACO (F81-P08).

### REFERENCES

(1) Van Amstel, A. Methane. A review. *J. Integr. Environ. Sci.* 2012, 9, 5–30.

(2) Okafor, E. C.; Somarathne, K. D. K. A.; Rathnahan, R.; Hayakawa, A.; Kudo, T.; Kurata, O.; Iki, N.; Tsujimura, T.; Furutani, H.; Kobayashi, H. Control of NO, and other emissions in micro gas turbine combustors fuelled with mixtures of methane and ammonia. *Combust. Flame* 2020, 211, 406–416.

(3) Chen, L.; Qi, Z.; Zhang, S.; Su, J.; Somorjai, G. A. Catalytic hydrogen production from methane: A review on recent progress and prospect. *Catalysts* 2020, 10, No. 858.

(4) Yadav, V. G.; Yadav, G. D.; Patankar, S. C. The production of fuels and chemicals in the new world: critical analysis of the choice between crude oil and biomass vis-à-vis sustainability and the environment. *Clean Technol. Environ. Policy* 2020, 22, 1757–1774.

(5) Wang, B.; Albarracin-Suazo, S.; Pagán-Torres, Y.; Nikolla, E. Advances in methane conversion processes. *Catal. Today* 2017, 285, 147–158.

(6) Kiani, D.; Sourav, S.; Baltrusaitis, J.; Wachs, I. E. Oxidative coupling of methane (OCM) by SiO₂-supported tungsten oxide catalysts promoted with Mn and Na. *ACS Catal.* 2019, 9, 5912–5928.

(7) Huang, K.; Miller, J. B.; Huber, G. W.; Dumesic, J. A.; Maravelias, C. T. A general framework for the evaluation of direct nonoxidative methane conversion strategies. *Joule* 2018, 2, 349–365.

(8) Keller, G. E.; Bhasin, M. M. Synthesis of ethylene via oxidative coupling of methane I. Determination of active catalysts. *J. Catal.* 1982, 73, 9–19.

(9) Fleischer, V.; Steuer, R.; Parishan, S.; Schomäcker, R. Investigation of the surface reaction network of the oxidative coupling of methane over Na₂WO₄/Mn/SiO₂ catalyst by temperature programmed and dynamic experiments. *J. Catal.* 2016, 341, 91–103.

(10) Gambo, Y.; Jalil, A. A.; Triwahyono, S.; Abdulraheem, A. A. Recent advances and future prospect in catalysts for oxidative coupling of methane to ethylene: A review. *J. Ind. Eng. Chem.* 2018, 59, 218–229.

(11) Alvarez-Galvan, M. C.; Mota, N.; Ojeda, M.; Rojas, S.; Navarro, R. M.; Fierro, J. L. G. Direct methane conversion routes to chemicals and fuels. *Catal. Today* 2011, 171, 15–23.

(12) Kidamorn, P.; Tiyatha, W.; Chukeaw, T.; Niamnuy, C.; Chareonpanich, M.; Sohn, H.; Seubsai, A. Synthesis of value-added chemicals via oxidative coupling of methane over Na₂WO₄-TiO₂-MnO₂/SiO₂ catalysts with alkali or alkali earth oxide additives. *ACS Omega* 2020, 5, 13612–13620.

(13) Chukeaw, T.; Sringam, S.; Chareonpanich, M.; Seubsai, A. Screening of single and binary catalysts for oxidative coupling of methane to value-added chemicals. *Mol. Catal.* 2019, 470, 40–47.

(14) Sringam, S.; Kidamorn, P.; Chukeaw, T.; Chareonpanich, M.; Seubsai, A. Investigation of metal oxide additives onto Na₂WO₄/TiO₂/SiO₂ catalysts for oxidative coupling of methane to value-added chemicals. *Catal. Today* 2020, 358, 263–269.

The authors declare no competing financial interest.

**Notes**
(15) Amenomiya, Y.; Birss, V. I.; Goledzinowski, M.; Galuszka, J.; Sanger, A. R. Conversion of methane by oxidative coupling. Catal. Rev. 1990, 32, 163–227.

(16) Xu, J.; Zhang, Y.; Xu, X.; Fang, X.; Xi, R.; Liu, Y.; Zheng, R.; Wang, X. Constructing LaBₓO₃ (B = Ti, Zr, Ce) compounds with three typical crystalline phases for the oxidative coupling of methane: The effect of phase structures, superoxide anions, and alkalinity on the reactivity. ACS Catal. 2019, 9, 4030–4045.

(17) Sollier, B. M.; Bonne, M.; Khenoussi, N.; Michelin, L.; Miró, E. E.; Gómez, L. E.; Boix, A. V.; Lebeau, B. Synthesis and characterization of electrospun nanofibers of Sr-La-Ce oxides as catalysts for the oxidative coupling of methane. Ind. Eng. Chem. Res. 2020, 59, 11419–11430.

(18) Sim, Y.; Kwon, D.; An, S.; Ha, J.-M.; Oh, T.-S.; Jung, J. C. Catalytic behavior of ABO₃ perovskites in the oxidative coupling of methane. Mol. Catal. 2020, 489, No. 110925.

(19) Song, J.; Sun, Y.; Ba, R.; Huang, S.; Zhao, Y.; Zhang, J.; Sun, Y.; Zhu, Y. Monodisperse Sr–La₂O₃ hybrid nanofibers for oxidative coupling of methane to synthesize C₂ hydrocarbons. Nanoscale 2015, 7, 2260–2264.

(20) Kwon, D.; Yang, J.; An, S.; Cho, J.; Ha, J.-M.; Jung, J. C. A study on active sites of A₂BO₄ catalysts with perovskite-like structures in oxidative coupling of methane. Mol. Catal. 2021, 506, No. 111548.

(21) DeBoy, J. M.; Hicks, R. F. Oxidative coupling of methane over alkaline earth promoted La₂O₃. J. Chem. Soc., Chem. Commun. 1988, 982–984.

(22) Jiang, T.; Song, J.; Huo, M.; Yang, N.; Liu, J.; Zhang, J.; Sun, Y.; Zhu, Y. La₂O₃ catalysts with diverse spatial dimensionality for oxidative coupling of methane to produce ethylene and ethane. RSC Adv. 2016, 6, 34872–34876.

(23) Uphade, B. S.; Mulla, S. A. R.; Choudhary, V. R. Influence of metal oxide-support interactions in supported La-promoted CaO catalysts for oxidative coupling of methane. Stud. Surf. Sci. Catal. 1998, 113, 1015–1021.

(24) Choudhary, V. R.; Mulla, S. A. R.; Uphade, B. S. Oxidative coupling of methane over supported La₂O₃ and La-Promoted MgO Catalysts: Influence of catalyst–support interactions. Ind. Eng. Chem. Res. 1997, 36, 2096–2100.

(25) Lim, S.; Choi, J.-W.; Jin Suh, D.; Lee, U.; Song, K. H.; Ha, J.-M. Low-temperature oxidative coupling of methane using alkaline earth metal oxide-supported perovskites. Catal. Today 2020, 352, 127–133.

(26) Elkins, T. W.; Roberts, S. J.; Hagelin-Weaver, H. E. Effects of alkali and alkaline-earth metal dopants on magnesium oxide supported rare-earth oxide catalysts in the oxidative coupling of methane. Appl. Catal., A, 2016, 528, 175–190.

(27) Yamashita, H.; Machida, Y.; Tomita, A. Oxidative coupling of methane with peroxide ions over barium-lanthanum-oxygen mixed oxide. Appl. Catal., A, 1991, 79, 203–214.

(28) Hou, Y.-H.; Han, W.-C.; Xia, W.-S.; Wan, H.-L. Structure sensitivity of La₂O₃CO₃ catalysts in the oxidative coupling of methane. ACS Catal. 2015, 5, 1663–1674.

(29) Yusof, S. M.; Othaman, R.; Setiabudi, H. D.; Teh, L. P. Modified fibrous silica for enhanced carbon dioxide adsorption: Role of metal oxides on physicochemical properties and adsorption performance. J. Solid State Chem. 2021, 294, No. 121845.

(30) Papa, F.; Luminta, P.; Osiceanu, P.; Birjega, R.; Akane, M.; Balint, I. Acid–base properties of the active sites responsible for C₂⁺ formation and CO₂ formation over MO–Sm₂O₃ (M=Zn, Mg, Ca and Sr) mixed oxides in OCM reaction. J. Mol. Catal. A: Chem. 2011, 346, 46–54.

(31) Zavyalova, U.; Holena, M.; Schlägl, R.; Baerns, M. Statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts. ChemCatChem 2011, 3, 1935–1947.

(32) Yingli, B.; Kaiji, Z.; Yutao, J.; Chiwen, T.; Xiangguong, Y. Catalytic oxidative coupling of methane over alkali, alkaline earth and rare earth metal oxides. Appl. Catal. 1988, 39, 185–190.

(33) Petrolini, D. D.; Marcos, F. F. C.; Lucrédio, A. F.; Mastelaro, V. R.; Assaf, J. M.; Assaf, E. M. Exploiting oxidative coupling of methane performed over La₂(Ceₓ−ₓMgx)₁O₇−ₓ catalysts with disordered defective cubic fluorite structure. Catal. Sci. Technol. 2021, 11, 4471–4481.

https://doi.org/10.1021/acsomega.1c04738
ACS Omega 2022, 7, 1785–1793