Investigation of perovskite catalysts BaTiO₃ and SrTiO₃ for the oxidative coupling of methane

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**ABSTRACT**

In this study, perovskite BaTiO₃ and SrTiO₃ catalysts were prepared using the sol-gel method for oxidative coupling of methane (OCM). Characterization of catalysts was investigated by X-ray diffraction for crystal properties, physical N₂ adsorption to determine specific surface area, and temperature-programmed techniques to examine the redox properties and acid–base strength. The results showed that at any reaction temperature, the methane conversion of BaTiO₃ was consistently higher than that of SrTiO₃. This may caused by BaTiO₃’s better reducibility detected by H₂-TPR experiments. Moreover, the selectivity of BaTiO₃ (25 – 30%) was much greater than that of SrTiO₃. Perhaps the abundant lattice oxygen may explain the excellent C₂H₄ selectivity obtained for BaTiO₃.

**1. Introduction**

Methane is a simple gas used extensively to prepare syngas as an indirect path to produce many important chemical blocks [1 - 3]. In order to seek a more sustainable way of utilizing methane, direct conversion of methane to valuable compounds, particularly oxidative coupling of methane for production, such as ethane, ethylene, etc. has attracted much attention from both scientists and manufacturers worldwide. Because of methane’s highly stable C – H bond, the OCM reaction must undergo severe conditions such as elevated temperature or high pressure to extract H from methane to prepare methyl radicals, which coupled to form ethane afterward [4,5].

Perovskite, with an ABO₃ formula, where A can be lanthanum, alkali, or alkaline earth metals, and B denotes transition metals, respectively, have been researched widely for the application in oxidative coupling of methane because of their thermal stability, definite structure, high oxygen mobility ... [6]. Both BaTiO₃ and SrTiO₃ have excellent properties suitable for OCM reactions. Therefore, many reports have been published about their catalytic performance over the years. In 2012, based on the BaTiO₃ ‘s excellent activity, M. Gharibi and his co-workers employed BaTiO₃ as a model sample to investigate the catalytic mechanism and found that the lattice oxygen vacancies could be formed at low energy and only one active site was responsible for the reaction [7]. Significantly, the combination of BaTiO₃ and Mn-NaWO₄ had good results as higher activity at 100 °C lower than used for Mn-NaWO₄ which has been known as the best catalyst for OCM until now [8].

Since the advantage of developing the properties led to enhancing the catalytic performance, doping in SrTiO₃ has often been studied recently [9, 10]. The results showed that the oxygen mobility and electron transfer...
were well-improved; consequently, the methane conversion and C₂ selectivity also increased.

In Seoyeon Lim’s work [11], BaTiO₃ and SrTiO₃ were studied for OCM reaction, and it was reported that BaTiO₃ had better performance than SrTiO₃ at a temperature range from 600 °C to 725 °C under a gas mixture of (CH₄)/(O₂)/(N₂) = 3/1/1 (mol/mol/mol) with gas-hour space velocity of 10,000 h⁻¹. However, the XPS, CO₂-TPD, and O₂-TPD results did not explain clearly the relationship between perovskites’ properties and OCM reaction performances. Thus, this paper was expected to reveal this relationship more evidently.

In this paper, the perovskites BaTiO₃ and SrTiO₃ were prepared by sol-gel and investigated to determine their structure, redox properties, and acid–base strength, remarkably influencing the catalytic activity. Moreover, the OCM reaction was set up at harsh conditions such as high velocity (50,000 h⁻¹), high reaction temperatures (750 °C – 850 °C), and high gas mixture in which a molar ratio of (CH₄)/(O₂)/(N₂) = 4/1/80 (mol/mol/mol) that has not been reported yet. Likewise, it was strongly desired to discover more properties of BaTiO₃ and SrTiO₃ at high reaction temperatures and velocities to understand these perovskites completely.

2. Experimental

Materials

Ethylene glycol (HOCH₂CH₂OH, 99.8%), Barium nitrate (Ba(NO₃)₂, Sigma Aldrich) Strontium nitrate (Sr(NO₃)₂, Sigma Aldrich), citric acid (C₆H₈O₇ 99.5%), Titanium isopropoxide (Ti[OCH(CH₃)]₃) 97%, Sigma Aldrich) were used to prepare perovskite catalysts.

Preparation of catalyst

Titanium isopropoxide (9.15 mL) was dissolved in ethylene glycol (26.9 mL) and stirred at 60 °C for 30 minutes to obtain a clear solution. DI water (20 mL) was added to titanium isopropoxide and ethylene glycol solution, then stirred at 80 °C for one hour. The solution was cloudy white. After that, citric acid (25.8 g) was added to the solution at 80 °C to make a clear solution of yellow color during vigorous stirring. Then, Sr(NO₃)₂ (5.3 g) was added to the above solution and stirred until a viscous gel formed. Next, the gel was air-dried at 200 °C for 12 hours, and the resulting dry powder was calcined in air at 900 °C for 5 hours at a rate of 3 °C/min. Perovskite BaTiO₃ was prepared using the same procedure as described above.

Characterization

X-ray powder diffraction (XRD) investigated the samples’ crystalline phase. Using Bruker AXS D8 Advance XRD-diffractometer (Germany) with Cu Kα irradiation (40kV, 40 mA), XRD patterns were obtained. The Brunauer-Emmett-Teller (BET) method obtained the specific surface area using a Micromeritics (Gemini VII analyzer). In order to determine the reducing capacity of the oxide surface and the inhomogeneity of the reducing surface, the H₂-TPR measurement is used. Temperature-programmed oxygen desorption (O₂ - TPD) is analyzed to quantify the amount and strength of adsorbed oxygen species. NH₃ determined the acid-base properties – TPD and CO₂ – TPD experiments. The TPx method was analyzed using the Micromeritics Auto Chem II 2920 instrument at Hanoi University of Science and Technology. SEM images were captured on JEOL Beneluex equipment in the GeViCat Center, Hanoi University of Science and Technology.

Measurement of catalytic activity

The catalytic performances were determined using a continuous flow reaction system under ambient pressure. For this purpose, catalyst powder (200mg) was granulated with 250 ± 450 μm under compressor pressure and placed between a quartz reactor (370 mm height, 5 mm ID). The components as methane (CH₄), oxygen (O₂), and nitrogen (N₂) were introduced to the reactor after passing through a mixer, and the total flow of this gas mixture was fixed at 105mL/min, corresponding to a gas-hourly space velocity (GHSV) of 50,000 h⁻¹ determined at 25 °C and 1.5 bar pressure. Catalysts were performed under a gas mixture of CH₄, O₂, N₂, in which molar ratio of (CH₄)/(O₂)/(N₂) = 4/1/80 (mol/mol/mol). The reactions were at 750 °C, 800 °C, and 850 °C, and the products were analyzed by Gas Chromatography (GC) online coupled with Thermo Conductivity Detector and Flame Ionized Detector on the TRACE GC ULTRA system.

The conversion of CH₄ was defined as:

\[ \text{Conv} (\%) = \frac{A_{\text{CH}_4} - A_{\text{CH}_4, \text{in}}} {A_{\text{CH}_4, \text{in}}} \times 100\% \]
Where: Conv (%): Conversion of CH$_4$

\[ A_{\text{CH}_4} \] : Area of bypass peak of CH$_4$

\[ A_{*\text{CH}_4} \] : Area of the remaining peak of CH$_4$ after the reaction

Concentrations of C$_2$H$_4$ were defined as:

\[ C_{\text{C}_2\text{H}_4} (\%) = \frac{A_{\text{C}_2\text{H}_4} \cdot C_{\text{C}_2\text{H}_4}^*}{A_{*\text{C}_2\text{H}_4} \cdot C_{\text{C}_2\text{H}_4}^*} \times 100\% \]

Where: \( C_{\text{C}_2\text{H}_4}^* \) was the concentration, and \( A_{\text{C}_2\text{H}_4}^* \) was the corresponding peak area of the standard gas flow C$_2$H$_4$

Concentrations of CO$_2$: Determined through a standard curve (Figure 1) between the concentration and the area of the corresponding GC peak. Based on the standard curve, the CO$_2$ concentration was calculated by the equation below:

\[ y = 2.72652 \times 10^{-7} \times x + 0.00599 \quad (R^2 = 0.998) \]

Where:

\( y \): CO$_2$ concentration (%)

\( x \): Area of CO$_2$ peak

Fig 1: Standard curve \%\text{CO}_2

C$_2$H$_6$ selectivity (\%) was defined as:

\[ C_{\text{C}_2\text{H}_6} (\%) = \frac{C_{\text{C}_2\text{H}_6}}{C_{\text{C}_2\text{H}_4} + C_{\text{CO}_2} + C_{\text{C}_2\text{H}_6}} \times 100\% \]

### 3. Results and discussion

**Characterization of catalysts**

The X-ray diffraction patterns of the catalysts synthesized by the sol-gel are shown in Figure 2. The results showed that in the SrTiO$_3$ sample, the diffraction peaks at 2θ angle are 22.76°, 32.38°, 39.94°, 46.46°, 52.4°, 57.74°, 67.78°, 72.5°, 77.12° corresponded to the crystal planes (100), (110), (111), (200), (210), (211), (220), (300), (310), (311) [12]. There were no impurities phase on XRD patterns, proving the successful preparation of perovskite catalysts.

Fig 2: XRD pattern of catalysts

The specific area of catalysts was determined, and the results showed that the SrTiO$_3$ sample has a higher surface area than BaTiO$_3$, 16 m$^2$/g and 8.98 m$^2$/g, respectively. SEM captured the surface of catalysts, and their images in Figure 3 displayed the rough surface with large clusters on both SrTiO$_3$ and BaTiO$_3$. These results were in agreement with the small specific area obtained by BET.

Hydrogen temperature-programmed reduction (H$_2$-TPR) was performed in the H$_2$ flow over 100 mg of the material to analyze the reducibility of catalysts. The signal corresponding to H$_2$ consumption was plotted against temperature and shown in Figure 4 a). Profile of sample SrTiO$_3$ without reduction peak was recorded at temperatures below 400 °C, the broad peak was seen at 575 °C, while the BaTiO$_3$ ’s profile had two separated desorption peaks at 444 °C and 639 °C. The reducibility of SrTiO$_3$ was the same as the results observed in the (01-084-0443) data of the SrTiO$_3$ compound having space group Pm-3m, which indicated the single-phased cubic perovskite structure of the prepared compound [13]. Besides, the characteristic peaks of BaTiO$_3$ at 2θ angle as 22.2°, 32.17°, 38.89°, 45.59°, 50.81°, 56.12°, 65.77°, 70.32°, 74.78°, 79.01° were assigned for the crystal planes (100), (110), (111), (200), (210), (211), (220), (300), (310), (311) [12]. There were no impurities phase on XRD patterns, proving the successful preparation of perovskite catalysts.

Fig 3: SEM images of catalysts

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investigation of Lei Bai et al. [13]; in addition, the only possible reduction in this system was the reduction of titanium (Ti⁴⁺ → Ti³⁺) with simultaneous removal of oxygen from the perovskite structure [14]. As can be seen in Table 1, the amount of H₂ consumption on the SrTiO₃ (0.059 mmol/g) was approximate as the value of BaTiO₃ desorbed at 444 °C, 0.06 mmol/g; it seems like this desorption peak at 444 °C was also due to the reduction of Ti.

Table 1: Quantification of H₂ consumption by peak integration of H₂-TPR profiles of catalysts

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<th>Sample</th>
<th>Temperature (°C)</th>
<th>Quantity (mmol/g)</th>
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<tr>
<td>BaTiO₃</td>
<td>444</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>639</td>
<td>0.132</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>575</td>
<td>0.066</td>
</tr>
</tbody>
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On the other hand, the BaTiO₃ had another desorption peak at 639 °C, which was noticed to reduce bulk lattice oxygen [10]. Thus, it can be noticed that BaTiO₃ had better reducibility than SrTiO₃ because of the lower reduction temperature of Ti and another reduction of bulk lattice oxygen that SrTiO₃ did not have.

The NH₃–based properties of catalysts were examined by TPRx, and the results are shown in Figure 4 c) and d). The NH₃ desorption peak was detected at 225 °C on SrTiO₃, which inferred that some weak acidic sites present on the catalyst surface. On the other hand, in the case of BaTiO₃, there were two NH₃ desorption peaks at 591 °C and 721 °C, accounting for mid-strong and strong acid sites [16]. The basicity of catalysts was evaluated by CO₂-TPD measurement, and the profiles are displayed in Figure 4 d). It is noticed that the desorption peaked at 550°C on the SrTiO₃ profile, meaning the presence of a mid-strong primary site, while another significant CO₂ evolution was observed at 700°C on the BaTiO₃ profile, which accounted for a strong basic site.

**Catalytic activity**

The catalysts were employed for the OCM reaction in the temperature range from 750 to 850 °C, and the performances are shown in Figures 5 a) and b). In Figure 5 a), as the reaction temperature increased, the CH₃’s conversion of SrTiO₃ went from 8% to 15%. Additionally, the BaTiO₃ rose from 14.5% to 16%. As can be seen in the H₂-TPR results, the better reducibility of BaTiO₃ was also explained for higher methane conversion than that of SrTiO₃. Moreover, it was fascinating to obtain the C₂H₄’s selectivity of BaTiO₃ ranged from 25 to 30%, while the SrTiO₃ was about 0.8% at 800 °C in Figure 5 b).

During the OCM reaction, alkaline sites converted the methane to the methyl radical. Therefore, mid-strong and strong basic sites were considered as the essentially active sites for selectively activating methane to C₂ hydrocarbon. According to CO₂-TPD results, SrTiO₃ and BaTiO₃ had these critical sites but with different strengths. As a result, these catalysts could convert methane at reaction temperatures from 750 to 850°C. Nonetheless, the alkaline sites originate from oxygen anions (O₂⁻, O₂²⁻, O³⁻) on the catalysts’ surface. These surface oxygen species were consumed and transformed into vacancies, which can be refilled from https://doi.org/10.62239/jca.2024.011
the gas phase or lattice oxygen [10]. As in H₂-TPR results, not only SrTiO₃ but also BaTiO₃ had available lattice oxygen, which could quickly fill vacancies and continue to produce the alkaline sites in the OCM reaction. Besides, the lattice oxygen species had another important role in determining the selectivity of the OCM reaction. It is said that the lattice oxygen species with different binding energies led to dissimilar products of the OCM reaction. In primary, the lattice oxygen species with high binding energy and weak binding to metal promoted the conversion of CH₄ to CO₂, subsequently to CO₂ with adsorbed surface O species. In addition, the lattice O species with moderate binding to metal and binding energy were responsible for producing C₂ products. According to the O₂− TPD profile of BaTiO₃, it can be noted that the lattice oxygen species at 729 and 869 °C were perhaps in the group that was suited to form C₂H₄ selectively. Indeed, the selectivity of C₂H₄’s BaTiO₃ ranged from 25 to 30 % during the OCM reaction.

On the other hand, the lattice oxygen species strongly bonded to metal, resulting in low catalytic activity because of its high stability; it seems like SrTiO₃ was this case. In fact, the C₂ selectivity of this catalyst was only 0.8% at any temperature reaction. Though there are not any O₂ evolution peak on the SrTiO₃ profile, the presence of lattice O species is still noted by the H₂ desorption peak at 575 °C, and this O species strongly bind to metal, leading to low selectivity. In conclusion, both methane conversion and C₂H₄ selectivity of SrTiO₃ were worse than that of BaTiO₃ because BaTiO₃ had better reducibility and significant lattice oxygen species than the remaining one.

4. Conclusion

Perovskite BaTiO₃ and SrTiO₃ catalysts were prepared and fully characterized to investigate their properties and explain their catalytic activities in OCM reactions. The formation of delicate crystalline phases was shown on the XRD patterns. These two perovskites had a cubic phase. The BET method determined and captured the perovskite surface using the SEM method. The specific area of BaTiO₃ was slightly higher than that of SrTiO₃, at 16 m²/g and 8.98 m²/g, respectively. In addition, the SEM images of two perovskites were consistent with the low BET area. From H₂-TPR results, the lower temperature of desorption peak at 444 °C was one of the strong points that proved BaTiO₃ has better reducibility than SrTiO₃. Consequently, BaTiO₃ always had higher methane conversion than SrTiO₃ at any reaction temperature. Furthermore, the CO₂− TPD results determined the mid-strong and strong basic sites of these perovskites, which confirmed the capacity of both BaTiO₃ and SrTiO₃ to activate methane. Regarding selectivity, the O₂− TPD was performed to elucidate the lattice O species, which was the critical factor for C₂ selectivity. In BaTiO₃’s profile, there were three evolution peaks at 372 °C, 729 °C, and 869 °C, while no peak in SrTiO₃’s profile. It is said that the desorption peak at 372 °C was accounted for adsorbed O species, which could quickly refill the oxygen vacancies, resulting in high CH₄ conversion through the oxygen cycle during the reaction. On the other hand, the desorption peaks at 729 °C and 869 °C were assigned for lattice O species having moderate binding energy and moderate binding to metal. Hence, these lattice O species were responsible for BaTiO₃’s high C₂H₄ selectivity as 25 % – 30 % when the temperature reaction ranged from 750 °C to 850 °C.

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