

Alkali and alkaline-earth metal promoted Dy₂O₃ catalysts for oxidative coupling of methane

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ABSTRACT

The oxidative coupling of methane (OCM) is a promising route for the direct production of C₂ hydrocarbons from natural gas. In this study, a series of Dy₂O₃-based catalysts promoted with alkali and alkaline-earth metals (0.1MDy, M = Na, Ba, Sr) was synthesized via the wet impregnation method. Characterization results from XRD and FTIR confirmed the stability of the cubic Dy₂O₃ phase and the formation of surface carbonate species on the Ba and Sr-promoted catalysts. SEM-EDS analysis revealed a uniform distribution of alkaline earth metals on the support, whereas sodium was virtually undetected. Unlike traditional light rare-earth oxides that suffer from severe carbonate poisoning, the precisely tuned basicity of the Dy₂O₃ matrix facilitates a dynamic carbonate site-blocking mechanism. This unique structural advantage enables the promoted catalysts to effectively suppress deep oxidation even under a highly demanding, oxygen-rich environment (CH₄/O₂ = 4/1). At 800 °C, the alkaline earth metals confirmed their decisive role in directing the reaction toward hydrocarbon formation, with the 0.1BaDy catalyst achieving the maximum C₂ yield of 12.4%.

Keywords: OCM; Dy₂O₃; Methane; Oxidative coupling of methane; Rare Earth oxides; Ethylene.

1. INTRODUCTION

The continuous escalation of greenhouse gas (GHG) concentrations has rendered global warming an urgent challenge. Specifically, the Intergovernmental Panel on Climate Change (IPCC) projects that by 2050, total GHG emissions will surge to 2.35 times the levels recorded in 1996 [1]. Consequently, addressing this crisis necessitates the effective mitigation and processing of methane (CH₄), a primary constituent of GHGs. CH₄, the principal constituent of natural gas, is a primary greenhouse gas. Its conversion into ethylene – a widely used precursor in the polymer manufacturing [2] and petrochemical industries [3] – is of significant interest. The oxidative coupling of methane (OCM) is a promising direct pathway for this conversion, first reported by Keller, Bhasin, Hinsin, and Baerns [4]. In the reaction mechanism, methane undergoes partial oxidation, resulting in the abstraction of a hydrogen atom by an oxygen atom on the catalyst surface. The resulting methyl radical CH₃[•] desorbed from the catalyst surface, subsequently combines with another methyl radical in the gas phase to form ethane. The reaction proceeds with the dehydrogenation of ethane to yield ethylene [3-5].

1. $2\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O} \quad \Delta H_{298} = -87.8 \text{ kJ mol}^{-1}$
2. $2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298} = -140.4 \text{ kJ mol}^{-1}$
3. $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{298} = -801.3 \text{ kJ mol}^{-1}$
4. $2\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2\text{O} \quad \Delta H_{298} = -757 \text{ kJ mol}^{-1}$
5. $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad \Delta H_{298} = +137 \text{ kJ mol}^{-1}$

Given the developmental potential of the OCM reaction, the catalysts employed have garnered significant scientific interest. Over 30 years of intensive research in methane coupling, various catalysts have been evaluated, demonstrating improvements in the efficiency of methane conversion to C₂ hydrocarbons. Mn/NaWO₄/SiO₂ achieves high C₂ yields but requires operating temperatures of 800 °C [6]. Li/MgO Li/MgO shows high selectivity but is prone to deactivation due to Li⁺ volatilization [7]. Perovskite materials, with their ABO₃ crystal lattice structure, allow facile adjustment of elemental ratios but suffer from low surface area and structural instability [8]. In this context, rare-earth oxides (REOs) have emerged as one of the most promising catalysts for the OCM reaction. Consequently, REOs have emerged as promising catalysts due to their high oxygen mobility, stable oxidation states, and p-type conductivity at high temperatures [9]. While light REOs (La₂O₃, Nd₂O₃, Sm₂O₃) activate CH₄ below 700 °C [12-14], they often suffer from severe carbonate poisoning due to excessively strong intrinsic basicity. Recently, studies on Gd₂O₃ catalysts using N₂O as an oxidant have shown a very positive impact on C₂⁺ selectivity, achieving nearly 90% selectivity on a 0.1BaGd catalyst [15]. Furthermore, the presence of high-basicity elements is essential for directing product selectivity and preventing overoxidation. According to Juan Chen et al., the performance of REOs can be enhanced by using alkaline-earth metals as promoters [14].

Unlike light REOs, Dy₂O₃ exhibits moderate basicity due to lanthanide contraction, providing excellent structural stability but limiting initial methane activation. Therefore, this study strategically tunes the basicity of the Dy₂O₃ system using alkali and alkaline-earth metal promoters (Na, Ba, Sr) to facilitate a dynamic carbonate site-blocking mechanism, aiming to synergistically modulate active oxygen species and boost C₂ selectivity without compromising structural integrity. Furthermore, the utilization of the impregnation method facilitates a more homogeneous distribution of the elements, thereby preventing the severe agglomeration commonly associated with green rare-earth oxide synthesis routes [13].

2. EXPERIMENTAL

2.1. Precursor

Barium nitrate (Ba(NO₃)₂, purity ≥99.9%, Fluka Guarantee-Switzerland), strontium nitrate (Sr(NO₃)₂, purity ≥99.9%, Fluka Guarantee-Switzerland), sodium nitrate (NaNO₃, purity ≥99.9%, Fluka Guarantee-Switzerland), commercial dysprosium oxide (Dy₂O₃ ≥99.9%, Sigma-Aldrich-Germany), deionized water. All chemicals were used as received without further purification.

2.2. Synthesis procedure

Commercial Dy₂O₃ (≥ 99.9%, Sigma-Aldrich) was calcined at 800 °C for 5 h. The promoted catalysts (0.1MDy, M = Ba, Na, Sr) were synthesized via wet impregnation using Ba(NO₃)₂, NaNO₃, and Sr(NO₃)₂ (≥ 99.9%, Fluka) solutions to achieve a nominal atomic ratio of M/Dy = 0.1. The impregnated mixtures were dried, calcined at 800 °C for 5 h, ground, and sieved to 250 - 450 μm.

2.3. Experimental reaction testing

The experimental procedure was conducted at the GeViCat Catalysis Center (Building D8, Hanoi University of Science and Technology). OCM experiments were performed in a fixed-bed quartz reactor (Nabertherm furnace, Germany) using 0.2 g of catalyst. The feed gas stream, regulated by AALBORG mass flow controllers, comprised 35 vol% CH₄ in N₂ and 20 vol% O₂ in N₂ to obtain a total flow rate of 34.5 mL/min (GHSV = 10350 mL.(g.h)⁻¹). This maintains a CH₄/O₂ ratio of 4/1, an optimal range for REO catalysts [14, 15], providing an oxygen environment sufficient to cleave C-H bonds while protecting hydrocarbon products from deep oxidation [14]. Consequently, actual reactor concentrations were 24.35% CH₄ and 6.09% O₂, which kinetic studies indicate supply adequate molecular density to sustain methyl radical generation while ensuring efficient heat dissipation [16]. The reactants and products were analyzed online using a Thermo

Scientific Trace GC Ultra equipped with both a Flame Ionization Detector (FID) and a Thermal Conductivity Detector (TCD). The methane conversion (X_{CH_4}) and C_2 selectivity (S_{C_2}) were calculated based on the GC data using the following equations:

Methane conversion:

$$X_{CH_4}(\%) = \frac{n_{CH_4}^i - n_{CH_4}^o}{n_{CH_4}^i} \cdot 100 \quad (1)$$

Selectivity C_2 :

$$S_{C_2}(\%) = \frac{n_{C_2H_x}^o}{n_{C_2H_x}^o + n_{CO_x}^o} \cdot 100 \quad (2)$$

Yield C_2 :

$$Y_{C_2}(\%) = \frac{X_{CH_4} \times S_{C_2}}{100} \quad (3)$$

Where the subscripts “i” (inlet) and “o” (outlet) denote the molar flow rates of components at the reactor inlet and outlet, respectively. The term n represents the moles of each component, and C_2H_x and CO_x refer to the hydrocarbon products (C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8) and overoxidation products (CO_2 , CO) at the outlet.

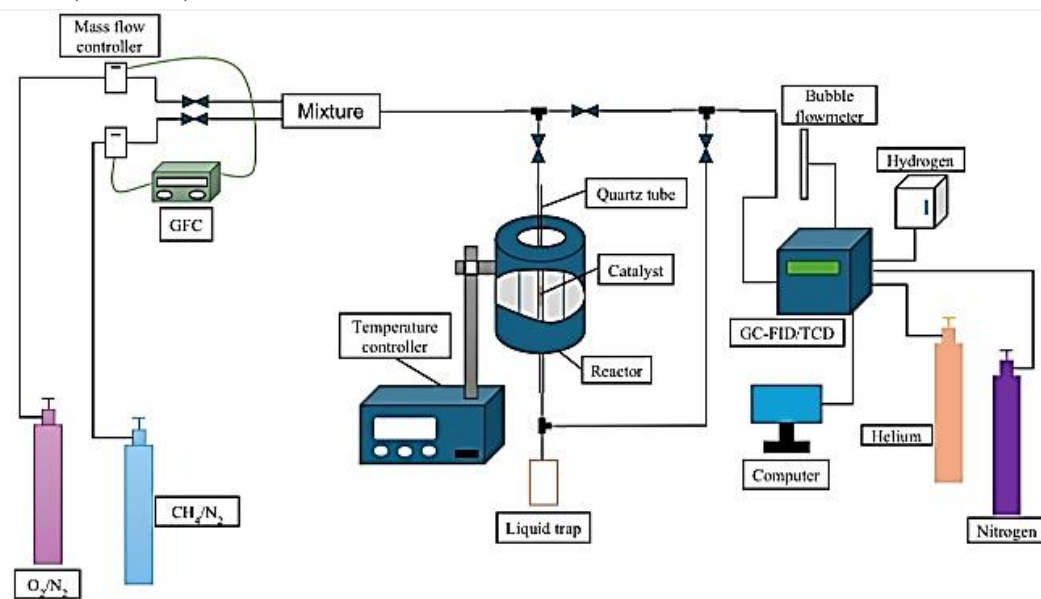


Figure 1. Schematic diagram of the experimental setup for the OCM reaction.

2.4. Catalyst characterization

The catalyst microstructure and morphology were characterized by Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) using a JEOL JCM-7000 instrument (JEOL, Japan).

The phase composition of the catalyst samples before and after the reaction was characterized by X-ray diffraction (XRD) on an X'Pert Pro Theta/Theta diffractometer (Panalytical) with $CuK\alpha$ ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA).

Fourier Transform Infrared Spectroscopy (FTIR) was utilized to identify the functional groups present in the catalyst samples. The spectra were recorded on a Nicolet iS50 FT-IR spectrometer within the wavenumber range of 4000 to 400 cm^{-1} .

The specific surface area and pore size distribution were determined from N₂ adsorption-desorption isotherms measured at 77 K using a Micromeritics Gemini VII analyzer. Before the measurements, the samples were degassed at 150 °C for 4 h to remove adsorbed moisture and impurities.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

FTIR spectra exhibited characteristic Dy-O bending vibrations at ~451 and 549 cm⁻¹ within the cubic Dy₂O₃ lattice [16, 17]. For the 0.1NaDy catalyst, the spectrum did not show significant differences compared to that of the bare Dy₂O₃, suggesting that the addition of sodium did not considerably alter the surface chemistry of the catalyst. In contrast, the 0.1BaDy and 0.1SrDy catalysts displayed new absorption bands in the 800-1500 cm⁻¹ region, indicating that the impregnation of Sr and Ba induced significant chemical modifications. Specifically, bands were observed at ~858.6 cm⁻¹ and ~1450.9 cm⁻¹ for the 0.1SrDy catalyst, and at ~692.6 cm⁻¹, ~857.5 cm⁻¹, and ~1434.3 cm⁻¹ for the 0.1BaDy catalyst. These signals are ascribed to the formation of carbonate species (CO₃²⁻) on the surface [19]. This finding suggests that the basicity of these materials was significantly enhanced - sufficiently strong to chemisorb atmospheric CO₂.

The phase composition and crystal structure of the fresh catalysts were investigated using X-ray diffraction (XRD). XRD patterns confirmed the highly crystalline cubic Dy₂O₃ phase (JCPDS 22-0612) in all fresh samples, evidenced by characteristic reflections of the (211), (222), (400), (411), (332), (431), (440), (611), (622), (631), and (444) planes [20]. The absence of secondary phases in 0.1NaDy and 0.1SrDy suggests the promoters are dispersed as amorphous sub-monolayers or integrated into the host lattice to form a solid solution [21]. This structural incorporation mechanism will be definitively validated by elemental atomic percentages in the forthcoming SEM-EDS and lattice parameter analyses.

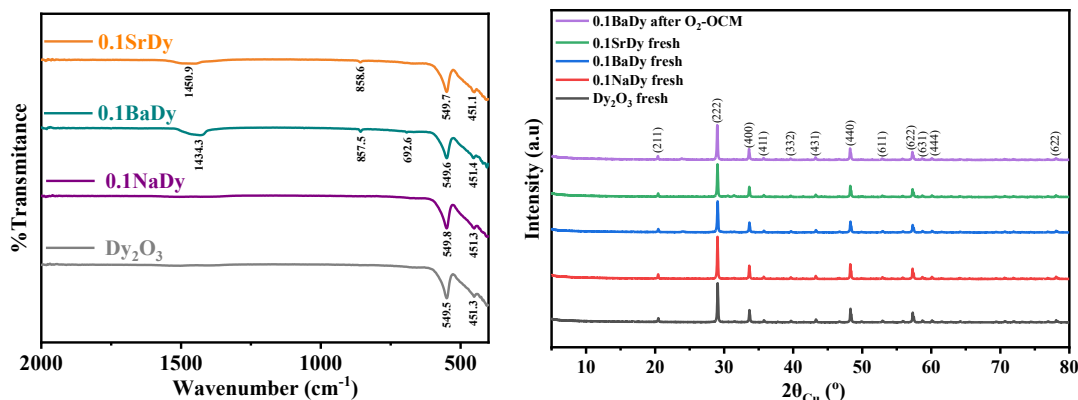


Figure 2. FTIR spectra and XRD patterns of the fresh catalysts and the 0.1BaDy catalyst after OCM reaction.

Conversely, the 0.1BaDy sample exhibited additional signals at $2\theta = 24^\circ, 24.3^\circ, 27.7^\circ$, and 42.2° , corresponding to BaCO₃ (JCPDS 05-0378) [22]. This observation aligns with the FTIR results and is attributed to the strong basicity of BaO, which readily reacts with atmospheric CO₂ during calcination. Post-reaction XRD of 0.1BaDy showed the primary cubic structure remained intact, demonstrating excellent thermodynamic stability under severe operating conditions.

SEM-EDS analysis (Table 1) and elemental mapping (Figure 3) confirmed the uniform dispersion of Ba and Sr across the Dy₂O₃ surface with atomic ratios closely matching nominal values. Conversely, 0.1NaDy showed a negligible surface Na signal. This physical absence, coupled with the lattice contraction of 0.1NaDy ($a = 10.555 \text{ \AA}$) compared to standard Dy₂O₃ ($a = 10.667 \text{ \AA}$) [21] indicates a deep structural integration. According to Shannon's ionic radii,

substituting Dy^{3+} (0.912 Å) with the larger Na^+ (1.020 Å) inherently necessitates the release of large O^{2-} anions for charge neutrality. The physical absence of these massive anions completely overshadows the cation expansion effect, thereby causing the entire unit cell to shrink. This deep incorporation explains why Na fails to populate the surface and adequately enhance basicity.

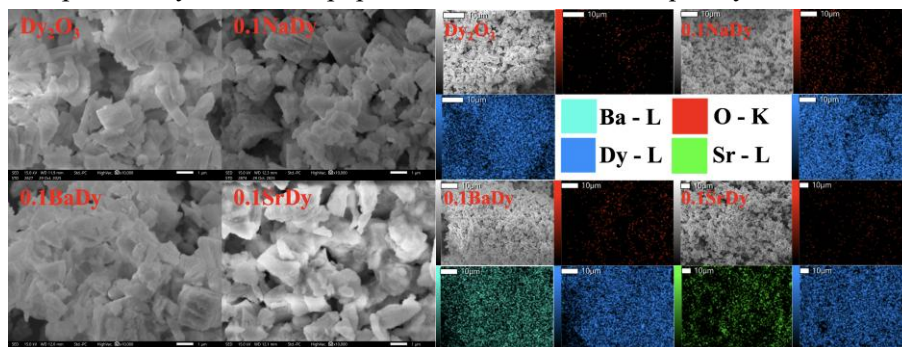


Figure 3. SEM morphologies and corresponding EDS elemental mapping images of the synthesized catalysts.

Table 1. Physicochemical properties and elemental composition of the synthesized catalysts.

Catalyst	%mol				Molar ratio M:Dy	S_{BET} (m^2/g)	d_{pore} (Å)
	Na	Ba	Sr	Dy			
0.1NaDy	0.59	-	-	68.71	0.009	1.37	413.26
0.1BaDy	-	5.53	-	50.18	0.11	0.45	190.44
0.1SrDy	-	-	4.61	45.41	0.1	1.75	332.69
Dy_2O_3	-	-	-	-	-	2.51	319.34

The physical properties of the synthesized catalysts, specifically the specific surface area (S_{BET}) and pore characteristics, were analyzed via N_2 physisorption. These results revealed a significant reduction in specific surface area for the promoted catalysts, dropping from $2.51 \text{ m}^2/\text{g}$ for pristine Dy_2O_3 to $0.45 \text{ m}^2/\text{g}$ for 0.1BaDy. This is attributed to enhanced sintering and pore-filling by large-radius cations during calcination. In the OCM reaction, this low surface area and mesoporous structure ($d_{\text{pore}} = 190 - 413 \text{ Å}$) serve as a strategic advantage by minimizing deep pores that prolong intermediate residence times and trigger secondary deep oxidation [23]. Furthermore, the introduction of additional strong basic sites via Na, Sr, and Ba promotion is recognized as a critical requirement for the efficient heterolytic activation of C-H bonds in methane [24]. The synergistic effect makes promoted Dy_2O_3 systems promising candidates for high-performance OCM applications.

3.2. Catalytic testing

Figure 4 illustrates the catalytic performance in the OCM reaction. The bare Dy_2O_3 catalyst exhibited moderate activity, reaching a maximum methane conversion of 14.3% and a C_2 selectivity of 56.8% at 800°C . In contrast, while the alkaline-earth-promoted catalysts showed negligible activity at 650°C , they exhibited a remarkable performance surge at 800°C . The methane conversion for 0.1BaDy and 0.1SrDy reached 18.4% and 17.5%, while C_2 selectivity significantly increased to 67.5% and 69.2%, respectively. This superior efficiency is attributed to the incorporation of alkaline earth metal ions into the Dy_2O_3 lattice, which proliferates oxygen vacancies and improves surface basicity. These synergistic effects facilitate the formation of active oxygen species (O_2^{2-} , O^-) that favor the selective formation of C_2 products [25, 26].

Conversely, the 0.1NaDy catalyst showed marginal improvement. As previously elucidated, smaller Na^+ ions predominantly diffused into the bulk lattice, failing to adequately enhance surface basicity or form a protective carbonate layer, which leaves unmasked electrophilic oxygen species

free to drive deep oxidation. The profound enhancement of 0.1BaDy and 0.1SrDy directly correlates with modulated basicity: strong basic sites trap by-product CO_2 to form surface carbonates. At the optimal temperature of 800 °C, this dynamic carbonate layer partially decomposes, effectively masking non-selective electrophilic oxygen sites to suppress deep oxidation, while maintaining moderate basic sites for continuous, selective C-H bond activation [27]. Consequently, 0.1SrDy exhibited the lowest CO_x formation (21.2% CO_2 , 9.5% CO).

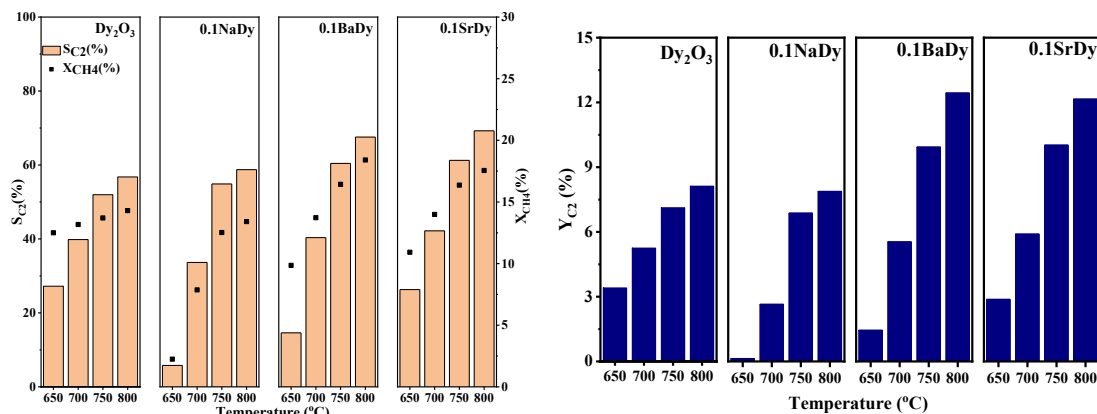


Figure 4. Survey of the activity of catalysts in the OCM reaction. Reaction conditions: Flow rate = 34.5ml/min, $m_{cat} = 0.2\text{g}$, Concentration CH_4 : 35%, $T = 650, 700, 750, 800$ °C.

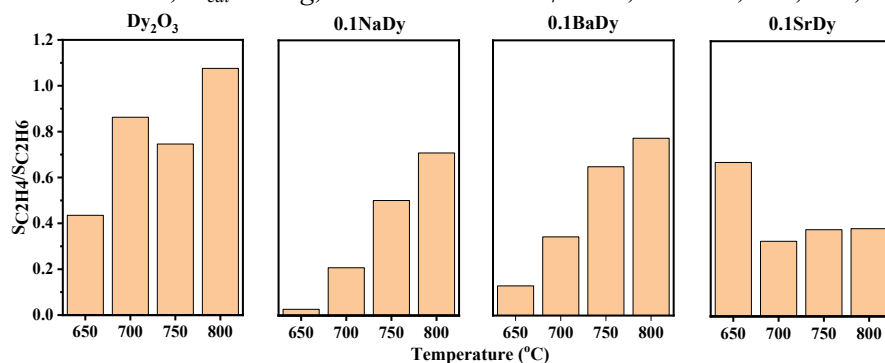


Figure 5. Effect of reaction temperature on $\text{Sc}_{\text{C}_2\text{H}_4}/\text{Sc}_{\text{C}_2\text{H}_6}$ ratio over the evaluated catalysts.

The $\text{Sc}_{\text{C}_2\text{H}_4}/\text{Sc}_{\text{C}_2\text{H}_6}$ ratio (Figure 5) evaluates the capacity to promote ethane dehydrogenation to ethylene. This ratio increases linearly with temperature for Dy_2O_3 , 0.1NaDy, and 0.1BaDy, but drops significantly for 0.1SrDy at temperatures favorable for C_2 formation. While bare Dy_2O_3 achieves the highest ratio at 800 °C, it paradoxically yields the lowest C_2 selectivity. This phenomenon is attributed to highly active electrophilic oxygen species on the bare surface, which drive the deep oxidation of generated ethane into CO_x , thereby depleting the ethane pool and anomalously inflating the $\text{Sc}_{\text{C}_2\text{H}_4}/\text{Sc}_{\text{C}_2\text{H}_6}$ ratio.

The 0.1BaDy catalyst demonstrates an excellent mechanistic balance. Doping with barium effectively modulates surface basicity and suppresses the formation of diatomic oxygen species responsible for deep oxidation pathways [15]. Consequently, 0.1BaDy maintains a substantial total C_2 yield without severely compromising ethylene production. Its dehydrogenation capacity grows robustly from 0.12 at 650 °C to 0.77 at 800 °C. At 800 °C, absolute ethylene selectivity reaches an impressive 29.5%, allowing 0.1BaDy to achieve the optimal C_2 yield of 12.4% (18.5% methane conversion, 67.5% C_2 selectivity).

To contextualize the efficacy of the developed materials, their performance was benchmarked against typical REOs catalysts reported in previous literature. Conventional single REOs generally

exhibit modest C₂ yields under highly oxygen-deficient conditions (CH₄/O₂ = 8/1-9/1) at elevated temperatures (800-850 °C), as exemplified by La₂O₃ (Y_{C2} = 9.2%), Sm₂O₃ (Y_{C2} = 8.9%), Nd₂O₃ (Y_{C2} = 7.7%), Er₂O₃ (Y_{C2} = 5.2%), and Yb₂O₃ (Y_{C2} = 4.5%) [28], as well as Gd₂O₃ which only reaches a C₂ yield of 5.81% at a CH₄/O₂ ratio of 8/1 [15]. Even under slightly higher oxygen content (CH₄/O₂ = 7.2/1), CeO₂ exhibits a poor C₂ yield of 1.6% [16], while Ho₂O₃ provides a Y_{C2} of 9.7% [29]. Furthermore, an evaluation of other REO systems reveals that CeO₂, Tm₂O₃, and Tb₄O₇ (the latter requiring an even higher CH₄/O₂ ratio of 14.4/1 to circumvent deep oxidation) exhibit relatively low C₂ yields of 1.6%, 5.9%, and 7.8%, respectively [30]. In this context, the bare Dy₂O₃ catalyst in this study demonstrates a substantial intrinsic potential with a C₂ yield of 8.1% (X_{CH4} = 14.3%, S_{C2} = 56.8%) under a severe oxygen-rich environment (CH₄/O₂ = 4/1). Crucially, the alkaline-earth metal promotion in the 0.1BaDy system triggers a remarkable performance surge, achieving a superior C₂ yield of 12.4% (X_{CH4} = 18.4%, S_{C2} = 67.5%). The paramount advantage of the 0.1BaDy catalyst lies in its robust capacity to maintain high C₂ selectivity under demanding oxidizing conditions, where the Ba incorporation effectively modulates the density of active sites and lattice oxygen mobility to suppress parasitic oxidation pathways.

4. CONCLUSIONS

The 0.1MDy (M = Na, Ba, Sr) catalysts were successfully synthesized and evaluated for the OCM reaction. Physicochemical characterizations confirmed that alkaline earth metals (Ba, Sr) were uniformly dispersed on the support, enhancing surface basicity without altering the bulk cubic Dy₂O₃ structure. Mechanistically, promoting the moderate intrinsic basicity of Dy₂O₃ with strong Ba ions establishes a dynamic carbonate site-blocking layer. This precisely tuned basicity suppresses unselective electrophilic oxygen species, enabling the 0.1BaDy catalyst to achieve a maximum C₂ yield of 12.4% while thriving under severe oxygen-rich conditions (CH₄/O₂ = 4/1) at 800 °C. These findings provide a novel paradigm for strategically fine-tuning basicity in rare-earth oxide catalysts to prevent complete carbonate poisoning.

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TÓM TẮT**Xúc tác Dy_2O_3 biến tính kim loại kiềm và kiềm thổ cho phản ứng oxy hoá ghép đôi metan**

Oxy hoá ghép đôi metan (OCM) là một hướng đi đầy triển vọng để sản xuất trực tiếp etylen từ khí thiên nhiên. Trong nghiên cứu này, một loạt các chất xúc tác dựa trên Dy_2O_3 được biến tính bởi kim loại kiềm và kiềm thổ (0.1MDy , trong đó $M = \text{Na}, \text{Ba}, \text{Sr}$) đã được tổng hợp thông qua phương pháp tẩm ướt. Kết quả XRD và FTIR đã xác nhận tính ổn định của pha tinh thể Dy_2O_3 lập phương và sự hình thành nhóm chức cacbonat trên bề mặt của các chất xúc tác được mang lên bởi kim loại kiềm thổ. Phân tích SEM-EDS cho thấy sự phân bố đồng đều của kim loại kiềm thổ trên bề mặt chất mang, trong khi đó gần như không ghi nhận sự xuất hiện của Natri. Không giống như các oxit đất hiếm nhẹ truyền thống thường bị nhiễm độc cacbonat nghiêm trọng, độ kiềm được điều chỉnh chính xác của ma trận Dy_2O_3 tạo điều kiện thuận lợi cho cơ chế ngăn chặn vị trí cacbonat năng động. Ưu điểm cấu trúc độc đáo này cho phép các chất xúc tác được cải tiến có thể ngăn chặn quá trình oxy hóa sâu một cách hiệu quả ngay cả trong môi trường giàu oxy, đòi hỏi cao ($\text{CH}_4/\text{O}_2 = 4/1$). Ở 800°C , các kim loại kiềm thổ đã cho thấy khả năng định hướng phản ứng OCM tạo thành hydrocacbon, đặc biệt là xúc tác 0.1BaDy đạt hiệu suất C_2 là 12.4%.

Từ khoá: OCM; Oxit Đất Hiếm; Oxy hoá ghép đôi metan; Dy_2O_3 ; Metan; Etylen.