

Article

Effect of Acid-Controlled SBA-15 on Catalytic Performance of CaO/Cr-SBA-15 Dual-Functional Materials

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Abstract

Based on the acid-sensitive characteristics of SBA-15 during synthesis, this study varied the acid types, pH values, and mixed acid ratios during SBA-15 preparation to enhance the performance of CaO/Cr-SBA-15 dual-functional materials (DFMs) in integrated CO₂ capture and utilization for oxidative dehydrogenation of ethane (ICCU-ODHE). It was found that the SBA-15 support synthesized in an H₂SO₄ environment exhibited a high specific surface area and abundant surface silanol groups, which facilitated the dispersion of Cr and increased the proportion of Cr⁶⁺ active sites, thereby achieving the highest ethane conversion. In contrast, the moderate surface acidity of the HCl-prepared support facilitated the selective dehydrogenation of ethane over Cr active sites, effectively inhibiting side reactions and maximizing ethylene selectivity. Further investigations into the effects of pH and mixed acids revealed that pH 1 is optimal for SBA-15 preparation. At this value, the support reached its maximum mesoporous ordering and specific surface area, allowing for optimal Cr dispersion. Consequently, the ethane conversion, ethylene selectivity, and DFM yield all reached their peak values. Any deviation from this pH led to degradation of the support structure and reduced Cr dispersion, resulting in a significant decline in catalytic performance. Among the tested materials, the CaO/Cr-SBA-15-Cl-S DFM synthesized with an HCl-H₂SO₄ mixed acid demonstrated the superior reactivity, achieving an ethylene yield of 33.95%. Long-term cycling tests indicated that the material possesses good stability, with its performance attenuation primarily attributed to coking and adsorbent sintering.

Keywords: dual-functional materials; integrated CO₂ capture and utilization to-ethylene production; acid-controlled-SBA-15 synthesis; CO₂-oxidative dehydrogenation of ethane; Cr-based-catalysts



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1. Introduction

Ethylene serves as the cornerstone of the modern chemical industry, and its industrial scale is a key indicator of a nation's chemical sector development [1]. Traditional ethylene production predominantly relies on steam cracking and catalytic dehydrogenation technologies; however, these processes are universally plagued by significant drawbacks, most notably high energy consumption [2,3]. In contrast, the oxidative dehydrogenation of ethane with CO₂ (CO₂-ODHE) [4] has emerged as a highly promising alternative route,

owing to the mild oxidizing properties of CO₂. On one hand, CO₂-ODHE can overcome the thermodynamic limitations of ethane dehydrogenation, significantly promoting ethylene formation; on the other hand, it effectively inhibits the deep oxidation of ethylene, thereby enhancing reaction selectivity.

However, the conventional CO₂-ODHE process relies on a feed gas with stable CO₂ and ethane concentrations. In contrast, industrial CO₂ emissions are typically characterized by low concentrations and high impurity levels. Purifying such streams to the high concentrations required for the process, followed by compression, storage, and long-distance transportation, entails substantial capital expenditure and energy-intensive operations. This not only imposes a significant economic burden on the carbon capture stage but also diminishes the overall energy efficiency of the carbon circular economy due to the complex separation and purification procedures, ultimately hindering the large-scale industrial application of this technology.

Consequently, ICCU-ODHE has emerged as a promising solution [5–8]. First proposed by Rezaei et al. [9,10], this technology relies on DFMs—composed of calcium oxide-based sorbents and specific CO₂-ODHE catalysts [11,12]. This approach enables the integrated capture of industrial CO₂ and the co-production of ethylene, effectively bypassing the conventional stages of CO₂ purification, compression, and transportation, thereby significantly enhancing the economic viability of the process. Currently, research on ICCU-ODHE primarily focuses on the configuration of DFMs and the screening of catalyst types. Baamran et al. [13] investigated the impact of material arrangement within the DFM, demonstrating that a sequential configuration with the sorbent preceding the catalyst yields the optimal performance. Zhang et al. [14] screened four spinel catalysts, MgX₂O₄ (X = Cr, Ga, Fe, Al), combined with SolCaCe15 sorbents to form DFMs, verifying the feasibility of isothermal ICCU-ODHE at 650 °C. Additionally, Zhang et al. [15] revealed that the primary function of the calcium oxide-based sorbent within the DFM is CO₂ capture and release. In contrast, the catalytic activity and selectivity of the CO₂-ODHE reaction are predominantly determined by the performance of the incorporated catalyst. Consequently, the development of high-performance CO₂-ODHE catalysts represents a critical breakthrough point for enhancing the ethylene production efficiency and stability of the ICCU-ODHE process.

Cr-based catalysts represent a quintessential class of transition-metal catalysts and have been extensively utilized in the CO₂-ODHE [16]. Wei et al. [17] prepared CO₂-ODHE catalysts by loading Cr onto ZrO₂-modified γ -Al₂O₃, revealing that ZrO₂ modification facilitated the dispersion of Cr species, thereby increasing the abundance of surface Cr⁶⁺ species. Since Cr⁶⁺ species can be reduced to coordinatively unsaturated Cr³⁺ sites that serve as catalytically active centers [18], maximizing the surface concentration of Cr⁶⁺ is crucial for enhancing catalytic performance [19]. Numerous studies have demonstrated that the activity of Cr-based catalysts correlates with the relative content of surface Cr⁶⁺ [20]. Furthermore, the valence state of Cr is intrinsically linked to its dispersion on the support [21]; Cr species predominantly exhibit a +6 valence state when dispersed as single atoms or small nanoclusters [22]. Consequently, identifying suitable supports to achieve uniform Cr dispersion and thereby increase the proportion of Cr⁶⁺ represents an effective strategy for boosting the catalytic performance of Cr-based catalysts.

SBA-15 is considered an ideal support for Cr loading, as it offers abundant active sites for catalytic reactions and enhances catalyst dispersion [23,24]. Its highly ordered two-dimensional hexagonal mesoporous structure facilitates molecular diffusion in heterogeneous catalysis, while its thick pore walls endow SBA-15 with superior thermal stability [25]. Furthermore, surface silanol groups on SBA-15 can interact with metal ions during impregnation via coordination, condensation, or bridging to form Si-O-M covalent bonds, thereby improving the dispersion of metal ions [26]. The selection of SBA-15 as

the support for DFMs in this study is primarily based on its significant advantages over conventional supporting materials such as Al_2O_3 or zeolites. For the ICCU-ODHE, SBA-15 not only offers a higher specific surface area to ensure superior dispersion of active species but also possesses unique acid-sensitive characteristics that allow for precise control of pore properties and surface acid-base functionality by tuning the synthesis environment. Such tunability is essential for optimizing the distribution of Cr^{6+} active sites and enhancing the synergistic effect between the CaO adsorbent and catalytic centers. The structural characteristics and surface functional groups of SBA-15 are heavily influenced by synthesis parameters such as acid type [27], pH [28], crystallization temperature [29], and template agent [30]. This dependence arises because the formation of SBA-15 in solution follows the $(\text{S}^0\text{H}^+)(\text{X}^-\text{I}^+)$ mechanism [31]. In an acidic environment, tetraethyl orthosilicate (TEOS) hydrolyzes to generate protonated silica species. Meanwhile, the P123 template associates with anions (e.g., Cl^-). The template then attracts the protonated silica via electrostatic adsorption and hydrophilic-hydrophobic interactions, leading to ordered assembly into mesoporous structures [32]. Iga et al. [33] synthesized SBA-15 materials using TEOS as the silica source in various acidic media, including HCl, H_2SO_4 , HBr, and HNO_3 . Their findings revealed that different acids influence the pore structure, ordering, silanol distribution, and hydrothermal stability of the materials through factors such as counter-ion properties and hydration Gibbs free energy, thereby conferring specific application advantages. Although the type and amount of acid used during synthesis significantly impact the properties of SBA-15 supports, current research has largely focused on physical characteristics such as morphology and pore channels. There is a notable lack of studies investigating how the distinct properties of SBA-15 support affect the dispersion and catalytic performance of loaded Cr species. Therefore, a systematic investigation into the regulatory mechanisms by which the acidic environment modulates the properties of SBA-15 is of profound significance. Such insights enable the optimization of Cr dispersion and catalytic performance, which is essential for the rational design and construction of highly efficient Cr-based dual-functional materials.

In this study, we investigated the effects of four different acids (HCl, H_2SO_4 , H_3PO_4 , and HNO_3) used during synthesis on the structural properties, particle morphology, and surface functional groups of SBA-15. Furthermore, their impact on the dispersion of loaded Cr and on the performance of the resulting dual-functional materials (DFMs) was examined. We also evaluated the influence of pH on various characteristics of SBA-15 to determine the optimal synthesis pH. Based on these findings, SBA-15 was prepared using mixed acids to elucidate the mechanism by which acid anions influence the support. Finally, long-term cyclic tests were conducted on the DFMs to identify the causes of deactivation.

Therefore, this study investigated the effects of four different acids (HCl, H_2SO_4 , H_3PO_4 , and HNO_3) used during the preparation process on the structural properties, morphology, and surface functional groups of SBA-15. The CO_2 capture-conversion integration performance for ethylene production was compared among bifunctional materials composed of CaO mixed with Cr-SBA-15 catalysts synthesized via different acid routes. In addition, the effects of preparation parameters, such as pH and the mixed acid ratio, during SBA-15 synthesis were systematically explored. The long-cycle reaction performance of the bifunctional materials was evaluated, and their deactivation mechanism was elucidated.

2. Results and Discussion

2.1. Effect of Acid Type on Support Properties and DFM Performance

The small-angle XRD patterns of SBA-15 supports prepared with different acids are shown in Figure 1a. Using SBA-15-Cl as a reference, SBA-15-S exhibited distinct (100), (110), and (200) diffraction peaks without significant shifts. Its lattice constant was

comparable to that of SBA-15-Cl, indicating that SBA-15 prepared with H_2SO_4 maintained good structural ordering and crystallinity. In contrast, for SBA-15-N, the intensities of the (110) and (200) diffraction peaks were weak and nearly negligible. Moreover, the (100) diffraction peak showed a distinct shift, with 2θ increasing by 0.112 degrees. The lattice constant decreased by 1.13 nm compared to SBA-15-Cl, suggesting a decline in the structural ordering of the SBA-15 synthesized with HNO_3 . SBA-15-P exhibited a low-intensity (100) diffraction peak with a significant shift (2θ increased by 0.153 degrees), while the (110) and (200) peaks were completely absent. Additionally, SBA-15-P possessed the smallest lattice constant and crystallite size, at 8.55 nm and 1.26 nm, respectively. These results indicate that SBA-15 prepared using H_3PO_4 had the poorest crystallinity.

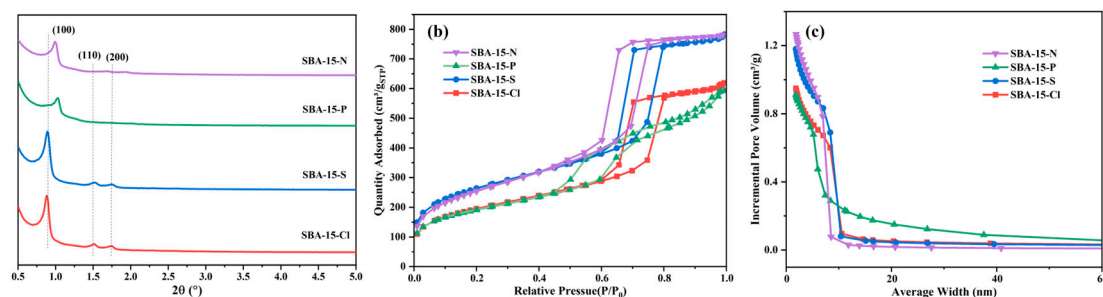


Figure 1. Structural characterization of SBA-15 supports prepared in different acidic media: (a) Small-angle XRD patterns, (b) N_2 adsorption–desorption isotherms, and (c) pore size distribution curves.

This phenomenon can be attributed to the primary role of the acid during SBA-15 preparation: catalyzing the hydrolysis of tetraethyl orthosilicate (TEOS) to generate protonated silica species. The hydrolysis rate of TEOS is dependent on the acidity of the solution [34]. Both HCl and H_2SO_4 are strong acids that dissociate completely in water, enabling them to catalyze the rapid hydrolysis of TEOS. Although HNO_3 is also a strong acid capable of complete ionization, it partially decomposes during hydrothermal crystallization, reducing the actual proton concentration in solution. Furthermore, the decomposition products of HNO_3 , such as O_2 and nitrogen oxides, may enter the reaction system, interfering with the hydrolysis of TEOS and the polymerization of protonated silica species. Among the four acids, H_3PO_4 has the weakest acidity, resulting in a relatively slow TEOS hydrolysis process. The hydrolysis reaction proceeds less thoroughly compared to strong acid systems, thereby affecting lattice formation and structural ordering. Consequently, different acids influence the TEOS hydrolysis rate due to variations in their acid strengths.

Figure 1b displays the N_2 adsorption–desorption isotherms and pore size distributions of SBA-15 prepared with the four acids. All supports exhibited Type IV isotherms with H1 hysteresis loops, indicating that all supports possessed mesoporous structures. Notably, the hysteresis loop of SBA-15-P showed a tendency to transition from Type H1 to Type H4, implying that the pore size distribution of SBA-15-P tended to be more dispersed, which is corroborated by the pore size distribution curve in Figure 2(c₁,c₂). Furthermore, the hysteresis loop of SBA-15-P shifted toward lower relative pressures, suggesting a shrinkage of the mesoporous channels. As shown in Table 1, SBA-15-P possessed the smallest maximum accessible pore diameter (5.511 nm) and average pore diameter (5.583 nm). Additionally, compared to the sample prepared with HCl , the specific surface areas of SBA-15 prepared with H_2SO_4 and HNO_3 increased from 675.209 m^2/g to 907.033 m^2/g and 895.206 m^2/g , respectively. Conversely, the specific surface area of SBA-15-P (658.801 m^2/g) was lower than that of SBA-15-Cl. The order of pore volume was as follows: SBA-15-N > SBA-15-S > SBA-15-P > SBA-15-Cl. These results demonstrate that the use of different acids during synthesis significantly alters the specific surface area and

pore structure of SBA-15 supports. The use of weakly ionizing acids, such as H_3PO_4 , in water is unfavorable for the formation of well-ordered mesoporous SBA-15 structures.

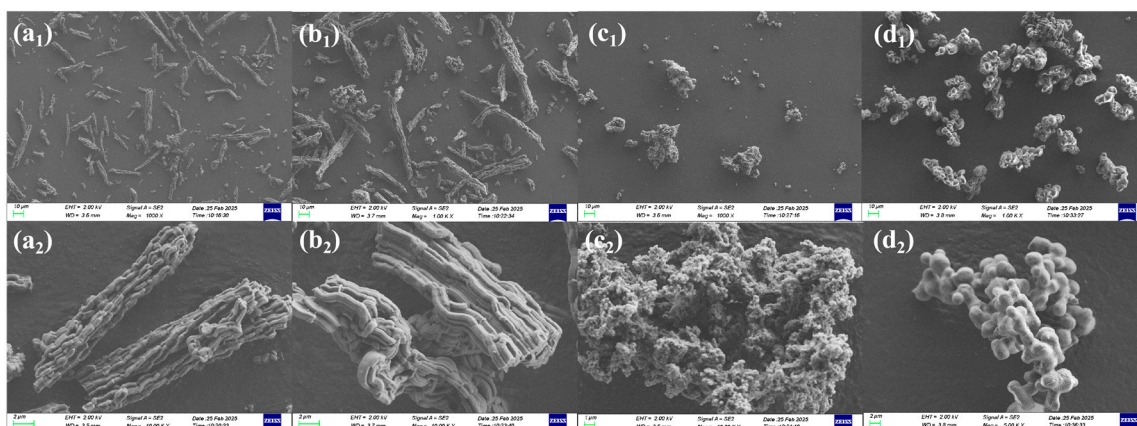


Figure 2. SEM images of the supports: (a₁,a₂) SBA-15-Cl; (b₁,b₂) SBA-15-S; (c₁,c₂) SBA-15-P; and (d₁,d₂) SBA-15-N.

Table 1. Textural parameters of SBA-15 supports synthesized with different acidic media.

Support	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)	Max Accessible Pore Diameter(nm)
SBA-15-Cl	675.209	0.949	5.694	9.172
SBA-15-S	907.033	1.180	5.359	9.126
SBA-15-P	658.801	0.912	5.583	5.511
SBA-15-N	895.206	1.267	5.421	7.550

The morphology of the four supports was investigated using SEM, as shown in Figure 2. It can be observed that SBA-15-Cl and SBA-15-S exhibited similar morphologies, characterized by rope-like particles. These particles were composed of numerous short, hexagonal prismatic rods stacked in parallel, which is consistent with the two-dimensional hexagonal mesoporous structure of SBA-15 reported in the literature [35]. Compared to SBA-15-Cl, the particles of SBA-15-S were longer, indicating that the SBA-15 prepared using H_2SO_4 possessed superior long-range ordering. The long-range ordering of SBA-15 particles depends on the balance between the rate of condensation of protonated silica species generated by TEOS hydrolysis and the rate of self-assembly between the template and silica species. When the rate of protonated silica condensation exceeds the self-assembly rate, it leads to the shrinkage of pore channels and a reduction in pore size. Conversely, when the condensation rate is slower than the self-assembly rate, although the P123 template can fully guide pore formation, the excessively fast self-assembly leads to insufficient skeletal strength, resulting in short rod-like or regular spherical particles. A rope-like mesoporous structure with good long-range ordering can only be formed when the two rates are matched and moderate [36]. The results suggest that when preparing SBA-15 with H_2SO_4 , the rate of condensation of protonated silica generated by TEOS hydrolysis was well-matched with the rate of self-assembly between the template and silica.

The particles of SBA-15-P and SBA-15-N were uniform in size and exhibited a regular spherical shape. The particle size of SBA-15-N was in the micrometer range, whereas that of SBA-15-P was in the nanometer range. The morphology of these two samples differed from the rope-like shape of SBA-15-Cl and SBA-15-S. This difference arises partly because the weaker acidity of HNO_3 and H_3PO_4 resulted in a TEOS hydrolysis rate that was slower than

the self-assembly rate, and partly due to the differences in anions. The formation of SBA-15 in solution follows the $(S^0H^+)(X^-I^+)$ mechanism [31], where anions in the solution adsorb onto the template and act as a bridge to assemble the protonated silica onto the template via electrostatic attraction. Different anions can alter the interaction strength between the protonated silica and the template due to factors such as ionic radius, charge density, and ionic structure, thereby affecting the particle morphology. The interaction between PO_4^{3-} and silanol groups is relatively strong, leading to a homogenization of the surface tension of the silica network, which causes the particles to structurally reorganize into spheres. Although NO_3^- does not possess as strong a coordination ability as PO_4^{3-} , the small N-O-N bond angle results in high bending energy at the silica-template interface, causing the particles to appear spherical on a macroscopic scale [37]. Additionally, its inherent oxidizing nature may also influence the TEOS hydrolysis process or the inorganic-organic self-assembly process. The particle size of SBA-15-P was smaller than that of SBA-15-N. This is because, despite partial decomposition, the acidity of HNO_3 is stronger than that of H_3PO_4 . Therefore, the rates of TEOS hydrolysis and silica partial condensation during crystallization were faster in the HNO_3 system than in the H_3PO_4 system, resulting in rapid particle growth and the formation of micrometer-sized particles for SBA-15-N. These results indicate that when preparing SBA-15 with different acids, the acid strength affects the rates of TEOS hydrolysis and protonated silica condensation, while different anions influence the bending energy at the protonated silica-template interface, thereby determining the particle morphology.

The types and quantities of functional groups on the surface of the prepared SBA-15 were quantitatively analyzed using solid-state ^{29}Si NMR, as shown in Figure 3 and Table 2. The results showed that compared to SBA-15-Cl, the number of silicon atoms in the Q3 structure $(OSi)_3Si(OH)$ on the surface of supports prepared with H_2SO_4 , H_3PO_4 , and HNO_3 increased significantly. Notably, SBA-15-S exhibited the largest increase of 26.5%. This indicates that, compared to the HCl system, the SBA-15 prepared with these three acids possessed more surface silanol groups. This is because SBA-15-S possessed the best long-range particle ordering, resulting in more silicon atoms on its surface being in a tetrahedrally coordinatively unsaturated state. In contrast, for SBA-15-P and SBA-15-N, the relatively poor mesoporous ordering prevented the formation of a highly cross-linked silica network. This resulted in numerous lattice defects, exposing more silicon atoms and leading to the formation of silanol groups, as evidenced by the small-angle XRD patterns of SBA-15-N and SBA-15-P in Figure 2a₁,a₂. In summary, the specific surface area, pore structure, particle morphology, and quantity of surface silanol groups of the SBA-15 supports vary significantly depending on the acid used for preparation.

The performance of isothermal integrated capture and conversion to ethylene using DFMs composed of the ethane oxidative dehydrogenation catalysts (prepared by loading Cr onto the aforementioned supports) and CaO was evaluated in the experimental setup. The results are presented in Figure 4. The ethane conversion rates in the first cycle for CaO/Cr-SBA-15-Cl, CaO/Cr-SBA-15-S, CaO/Cr-SBA-15-P, and CaO/Cr-SBA-15-N were 42.52%, 48.24%, 37.45%, and 43.69%, respectively. In the second cycle, these values decreased to 33.55%, 37.74%, 35.67%, and 31.26%, respectively.

Across the three cycles, the order of ethane conversion for the four DFMs was CaO/Cr-SBA-15-S > CaO/Cr-SBA-15-N > CaO/Cr-SBA-15-Cl > CaO/Cr-SBA-15-P. Under the steady-state conditions of the second and third cycles, the ethylene yields of CaO/Cr-SBA-15-Cl, CaO/Cr-SBA-15-S, and CaO/Cr-SBA-15-N were very similar. However, CaO/Cr-SBA-15-Cl exhibited the highest ethylene selectivity, reaching 82.0% and 79.8%, respectively.

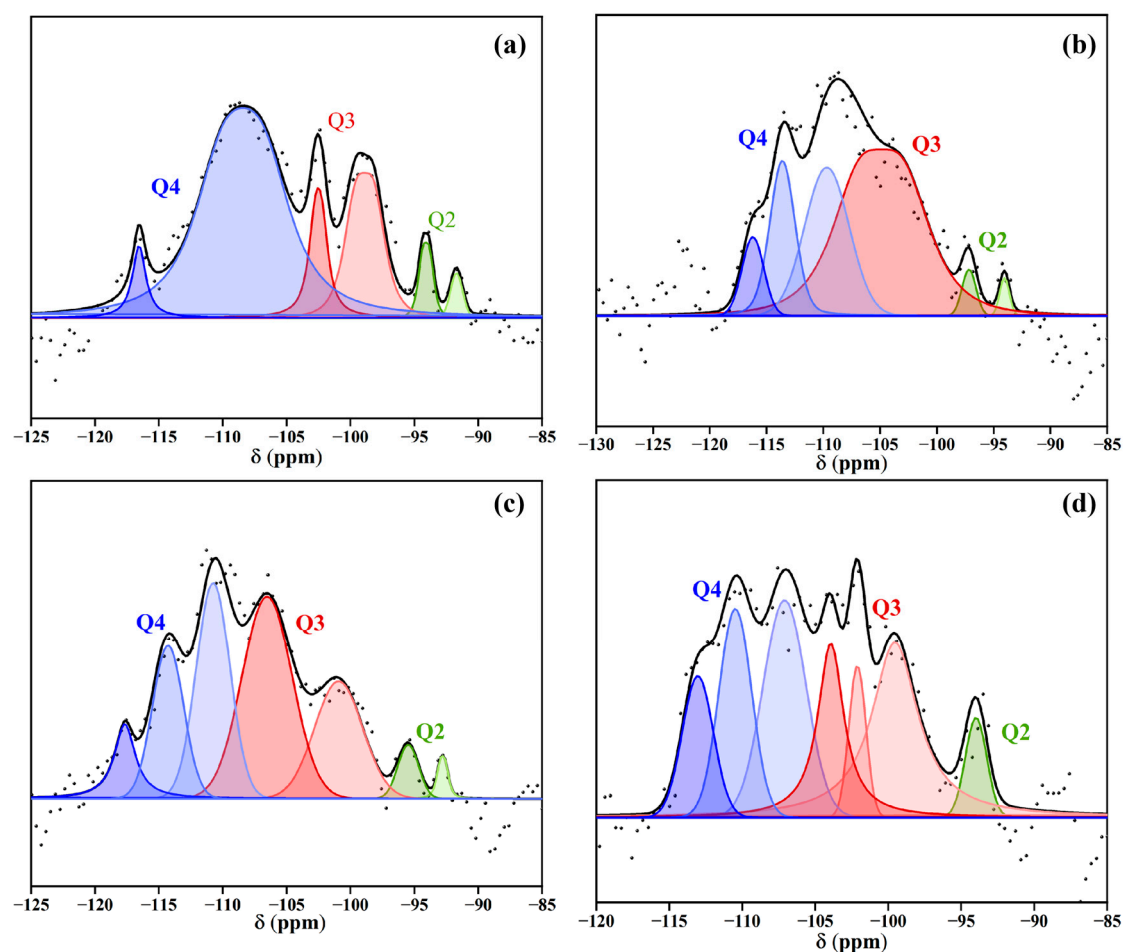


Figure 3. ^{29}Si NMR spectra of the supports: (a) SBA-15-Cl, (b) SBA-15-S, (c) SBA-15-P, and (d) SBA-15-N.

Table 2. Deconvolution results of ^{29}Si NMR spectra for the SBA-15 supports.

Support	Q2 (%)	Q3 (%)	Q4 (%)
SBA-15-Cl	5.1	26.4	69.5
SBA-15-S	3.5	52.9	43.6
SBA-15-P	5.1	49.5	45.4
SBA-15-N	4.8	48.8	46.4

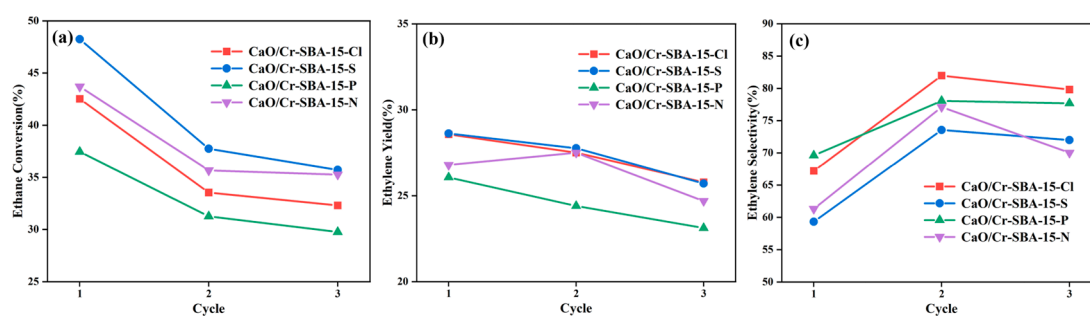


Figure 4. Cyclic catalytic performance of ethane oxidative dehydrogenation over CaO/Cr-SBA-15 DFMs prepared with different acidic media: (a) Ethane conversion, (b) Ethylene yield, and (c) Ethylene selectivity (Capture: 700 °C, 15 vol.% CO_2 , 30 mL/min, 30 min; Conversion: 700 °C, 4 vol.% C_2H_6 , 30 mL/min, 30 min).

The performance of the DFMs is related to the dispersion of Cr on the support surface. Therefore, XRD and Raman spectroscopy were used to compare the dispersion of Cr on SBA-15. No diffraction peaks corresponding to Cr_2O_3 were detected in the XRD patterns of the four catalysts shown in Figure 5a. In Figure 5b, the peak near 550 cm^{-1} represents the vibration of the Cr-O bond in Cr_2O_3 , where the peak area and intensity reflect the content of crystalline Cr_2O_3 . The peak near 1000 cm^{-1} corresponds to the vibration of the Si-O bond in SiO_2 [38]. It was observed that the Cr_2O_3 peak area for Cr-SBA-15-S was very small, indicating that the dispersion of Cr on Cr-SBA-15-S was the best. This is attributed to SBA-15-S having the largest specific surface area, regular pore channels, and the highest number of surface silanol groups. This suggests that the highest ethane conversion achieved by CaO/Cr-SBA-15-S results from its superior Cr dispersion, which facilitates the existence of more Cr species in the Cr^{6+} form. The Cr_2O_3 peak areas for Cr-SBA-15-P, Cr-SBA-15-N, and Cr-SBA-15-Cl showed little difference.

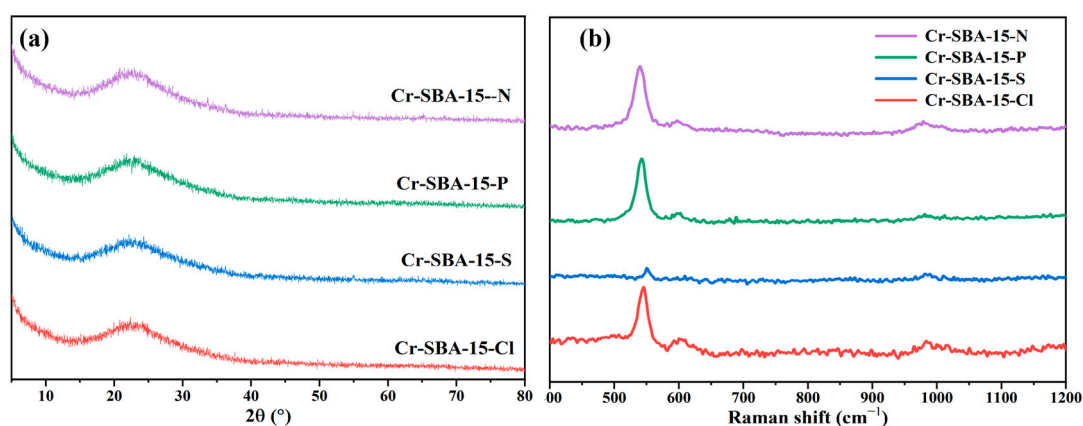


Figure 5. Comparison of Cr dispersion on SBA-15: (a) XRD patterns, (b) Raman spectra.

The O 1s XPS spectra of the catalysts are shown in the left column of Figure 6. Based on the binding energy, the oxygen species on the catalyst surface can be classified into three categories. The peak at approximately 530.5 eV represents oxygen in Cr oxides, denoted as OI [39]. Cr-SBA-15-S exhibited the highest proportion of OI (2.57%), indicating a higher oxidation state of Cr on the Cr-SBA-15-S surface, likely implying the presence of more Cr^{6+} species. The peak at approximately 532.9 eV corresponds to oxygen in the SiO_2 lattice and silanol groups, denoted as OII [40]. The peak at approximately 534 eV represents oxygen in adsorbed water, denoted as OIII [41]. This adsorbed water typically does not participate in the catalytic reaction and can be effectively removed by high-temperature pretreatment prior to testing. The right column of Figure 6 displays the Cr 2p XPS spectra of the catalysts, and the deconvolution results are summarized in Table 3. The peaks at binding energies of approximately 574 eV and 578 eV correspond to Cr^{3+} and Cr^{6+} in the Cr 2p spin-orbit, respectively. The results showed that the $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratios for Cr-SBA-15-Cl, Cr-SBA-15-S, Cr-SBA-15-N, and Cr-SBA-15-P were 1.436, 2.058, 0.773, and 1.560, respectively. Among them, Cr-SBA-15-S exhibited the highest $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio, indicating that it possesses the highest amount of Cr^{6+} species capable of being reduced to coordinatively unsaturated Cr^{3+} active sites. This aligns with the Raman results, confirming that Cr is most uniformly dispersed on the SBA-15-S surface, thereby resulting in the highest ethane conversion for CaO/Cr-SBA-15-S .

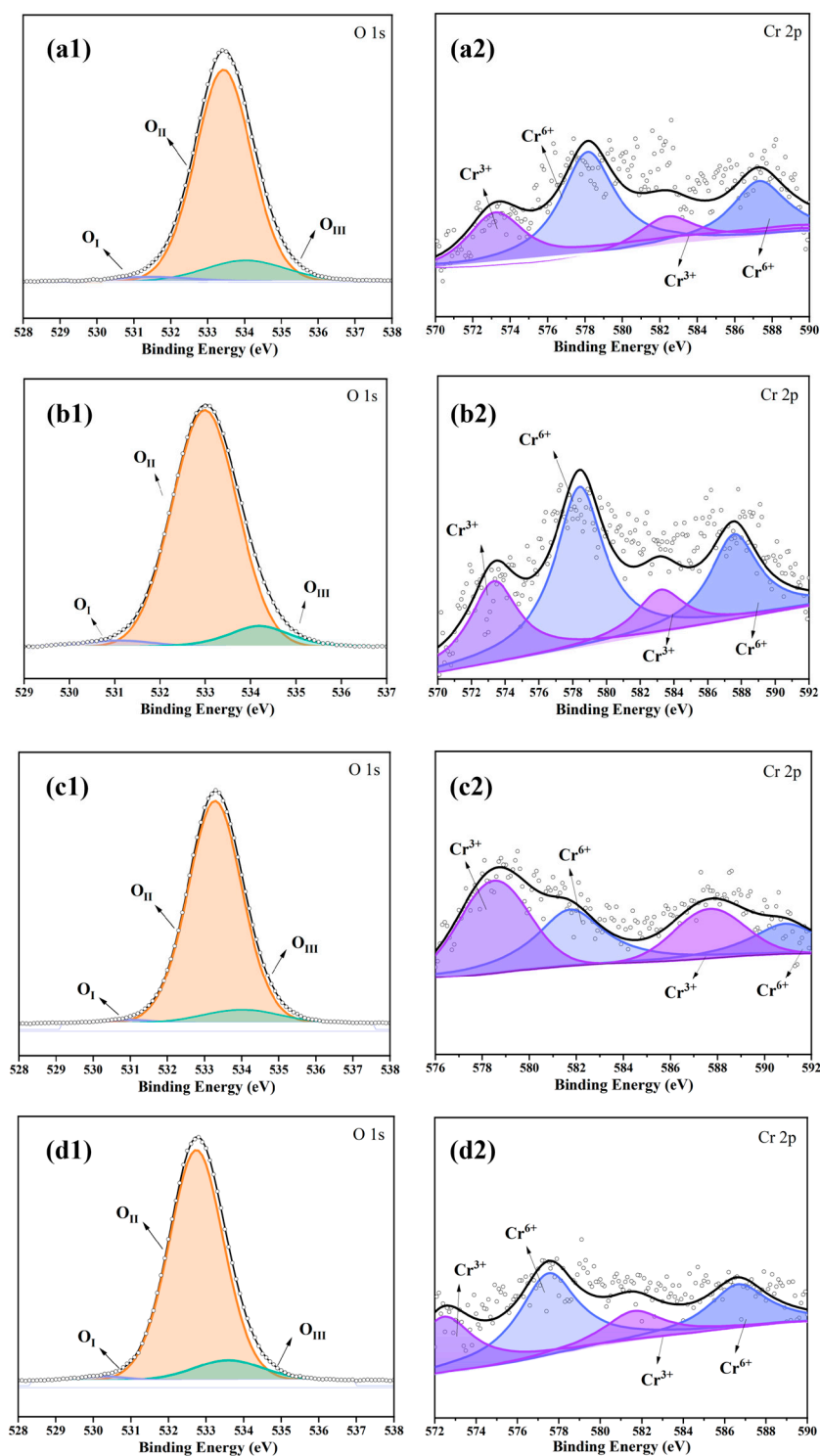


Figure 6. O 1s XPS spectra of the catalysts: (a1) Cr-SBA-15-Cl, (b1) Cr-SBA-15-S, (c1) Cr-SBA-15-P, (d1) Cr-SBA-15-N; and Cr 2p XPS spectra of the catalysts: (a2) Cr-SBA-15-Cl, (b2) Cr-SBA-15-S, (c2) Cr-SBA-15-P, (d2) Cr-SBA-15-N.

Table 3. XPS fitting parameters for O 1s and Cr 2p core levels of the catalysts.

Catalysts	O 1s Binding Energy (eV) and Area (%)						Cr 2p Binding Energy (eV) and Species Ratio		
	O _I (eV)	O _{II} (eV)	O _{III} (eV)	O _I (%)	O _{II} (%)	O _{III} (%)	Cr ³⁺ (eV)	Cr ⁶⁺ (eV)	Cr ⁶⁺ /Cr ³⁺
Cr-SBA-15-Cl	530.91	533.28	533.99	1.08	91.42	7.50	573.98	577.77	1.436
Cr-SBA-15-S	531.08	532.99	534.19	2.57	89.46	7.97	573.68	578.83	2.058
Cr-SBA-15-P	531.48	533.43	534.02	1.85	85.92	12.23	578.53	581.85	0.773
Cr-SBA-15-N	530.24	532.74	533.59	1.51	88.61	9.88	573.81	577.53	1.560

In summary, it can be concluded that the choice of acid used during the preparation of SBA-15 significantly influences the physicochemical properties of the support, which in turn affects the dispersion of loaded Cr species and the performance of the dual-functional materials. Specifically, the CaO/Cr-SBA-15-Cl prepared using HCl exhibited the highest ethylene selectivity, whereas the CaO/Cr-SBA-15-S prepared using H₂SO₄ achieved the highest ethane conversion. The use of HNO₃ resulted in a decrease in the mesoporous ordering of SBA-15 and altered the particle morphology. Conversely, the use of H₃PO₄ proved unfavorable for SBA-15 synthesis, as the resulting support exhibited severe lattice distortion and a lower pore volume. This led to the lowest proportion of surface Cr⁶⁺ species and, consequently, the poorest catalytic activity.

2.2. Effect of pH on Support Properties and DFM Performance

Given that the CaO/Cr-SBA-15-Cl dual-functional material exhibited the highest ethylene selectivity and superior overall performance, and that HCl avoids the introduction of residual foreign elements, the HCl system was selected to investigate the influence of different pH values during preparation. Figure 7a presents the small-angle XRD patterns of SBA-15 prepared at three different pH levels. It can be observed that SBA-15-Cl-1 and SBA-15-Cl-0.5 displayed three distinct characteristic diffraction peaks. In contrast, SBA-15-Cl-1.5 exhibited only a faint (100) diffraction peak, with the complete disappearance of the (110) and (200) peaks. This indicates that a solution pH below 1.5 is required for successful SBA-15 preparation. This is because the stable self-assembly of protonated silica species with the template requires a pH below the colloidal silica's isoelectric point (pH 2–3). When the pH approaches the isoelectric point, the net charge on the silica surface approaches zero, reducing electrostatic repulsion between particles. This not only facilitates particle agglomeration, disrupting the uniformity of protonated silica intermediates in the solution, but also weakens the interaction force between the silica species and the template, thereby leading to silica agglomeration [42].

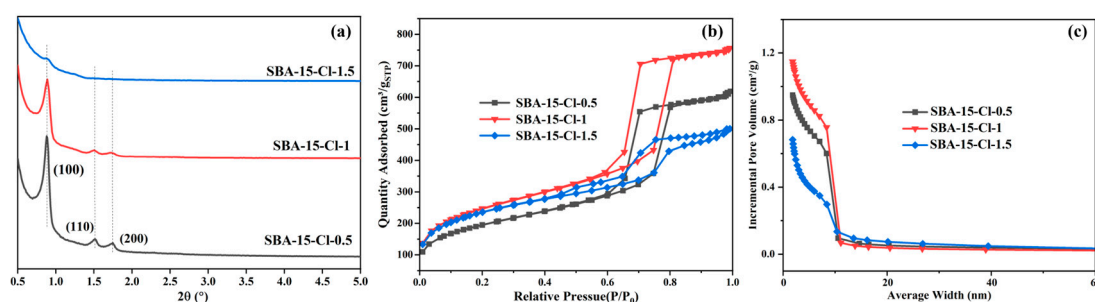


Figure 7. Structural characterization of SBA-15 supports prepared under different pH conditions: (a) Small-angle XRD patterns, (b) N₂ adsorption–desorption isotherms, and (c) pore size distribution curves.

As shown in Figure 7b, the N_2 adsorption–desorption curves of the supports all exhibited Type IV isotherms with H1 hysteresis loops, confirming that all supports possessed mesoporous structures. A comparison of the three samples reveals that the hysteresis loop of SBA-15-Cl-1.5 shifted toward lower relative pressure, indicating a contraction of the mesopores. As indicated in Table 4, both the average pore diameter and the maximum accessible pore diameter of SBA-15-Cl-1.5 were the smallest, at 3.673 nm and 9.159 nm, respectively. Moreover, the adsorption and desorption branches of the isotherm for SBA-15-Cl-1.5 did not fully coincide in the high relative pressure region, suggesting an inhomogeneous pore size distribution, which is further corroborated by the pore size distribution curve in Figure 7c. According to Table 4, SBA-15-Cl-1 exhibited the largest specific surface area ($887.356 \text{ m}^2/\text{g}$) and the largest pore volume ($1.174 \text{ cm}^3/\text{g}$). This demonstrates that for the preparation of SBA-15, a stronger acidity is not necessarily better. Instead, it is essential that the rates of the TEOS hydrolysis–silica condensation process and the inorganic–organic self-assembly process are comparable and moderate.

Table 4. Textural characteristics of SBA-15 supports synthesized at various pH values.

Support	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)	Max Accessible Pore Diameter (nm)
SBA-15-Cl-0.5	675.209	0.949	5.694	9.172
SBA-15-Cl-1	887.356	1.174	5.292	9.304
SBA-15-Cl-1.5	845.394	0.776	3.673	9.159

Significant differences were also observed in the morphologies of the three supports synthesized at different pH values, as depicted in Figure 8. It can be observed that the particles of SBA-15-Cl-0.5 and SBA-15-Cl-1 both appeared as short rods formed by the parallel stacking of hexagonal prismatic strips. In contrast, SBA-15-Cl-1.5 presented as irregular aggregates composed of accumulated spherical particles, characterized by rough surfaces with numerous wrinkles. The dimensions of the short rod-like particles of SBA-15-Cl-1 were significantly larger than those of SBA-15-Cl-0.5, indicating better structural regularity of SBA-15-Cl-1. The absence of rod-like morphology in SBA-15-Cl-1.5 is attributed to the synthesis pH approaching the isoelectric point of colloidal silica. Under these conditions, not only is the hydrolysis rate of tetraethyl orthosilicate (TEOS) retarded, but the protonation of silica species also becomes more difficult. Furthermore, the concentration of Cl^- in the solution decreases with increasing pH, hindering the template from guiding the assembly of silica species via electrostatic adsorption, thereby leading to silica agglomeration.

The catalytic performance of the three dual-functional materials—CaO/Cr-SBA-15-Cl-0.5, CaO/Cr-SBA-15-Cl-1, and CaO/Cr-SBA-15-Cl-1.5—was evaluated. Their ethane conversion, ethylene selectivity, and ethylene yield over three cycles are presented in Figure 9. Across the three cycles, the ethane conversion values for CaO/Cr-SBA-15-Cl-1 were 51.52%, 37.57%, and 34.05%; the ethylene selectivity values were 60.77%, 86.31%, and 89.16%; and the ethylene yields were 31.31%, 32.43%, and 30.36%, respectively. It is evident that CaO/Cr-SBA-15-Cl-1 exhibited the highest ethane conversion and ethylene yield. Moreover, it achieved the highest ethylene selectivity under the steady-state conditions of the second and third cycles. As indicated in Figure 10b, this superior performance is ascribed to the favorable dispersion of Cr on SBA-15-Cl-1. Better Cr dispersion leads to a higher abundance of surface Cr^{6+} species, thereby enhancing the performance of the dual-functional material.

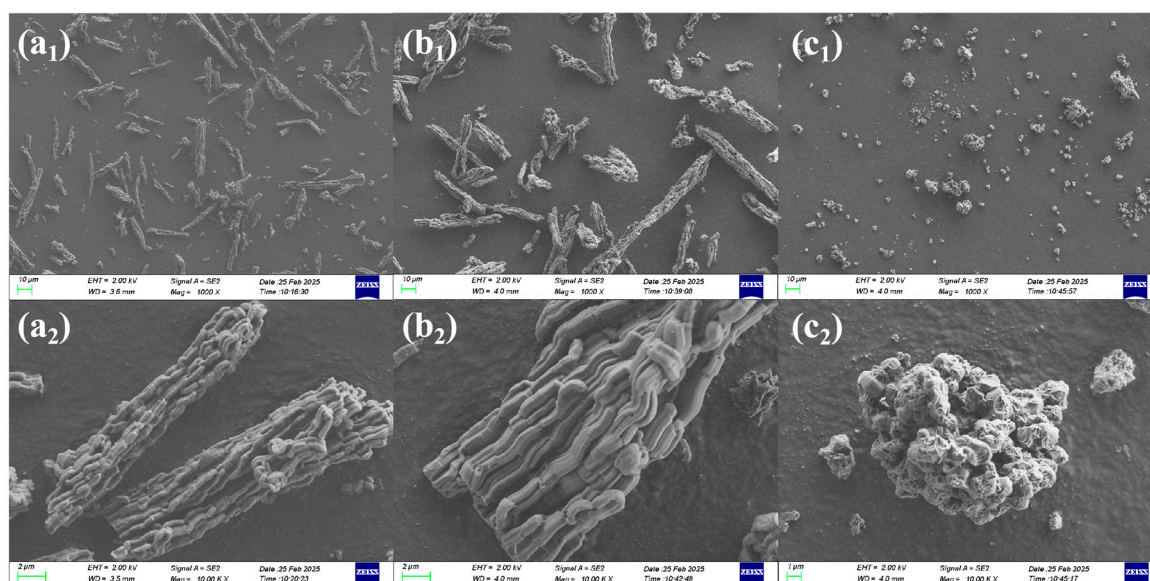


Figure 8. SEM images of the supports: (a₁,a₂) SBA-15-Cl-0.5; (b₁,b₂) SBA-15-Cl-1; and (c₁,c₂) SBA-15-Cl-1.5.

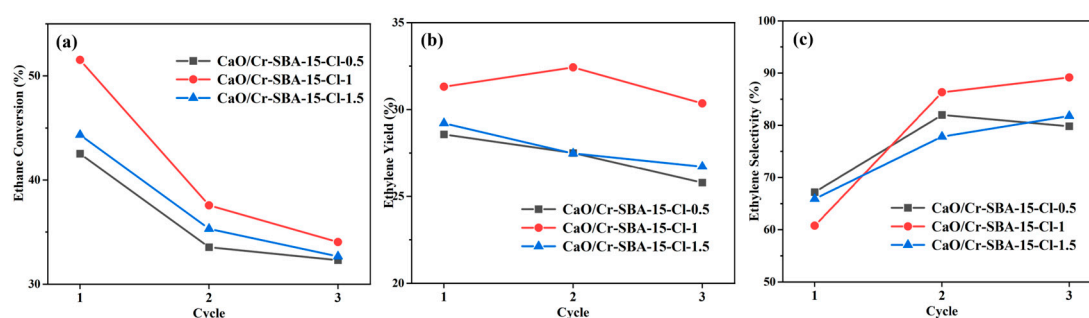


Figure 9. Cyclic catalytic performance of CaO/Cr-SBA-15-Cl-Y DFMs prepared under different pH conditions: (a) Ethane conversion, (b) Ethylene yield, and (c) Ethylene selectivity (Capture: 700 °C, 15 vol.% CO₂, 30 mL/min, 30 min; Conversion: 700 °C, 4 vol.% C₂H₆, 30 mL/min, 30 min).

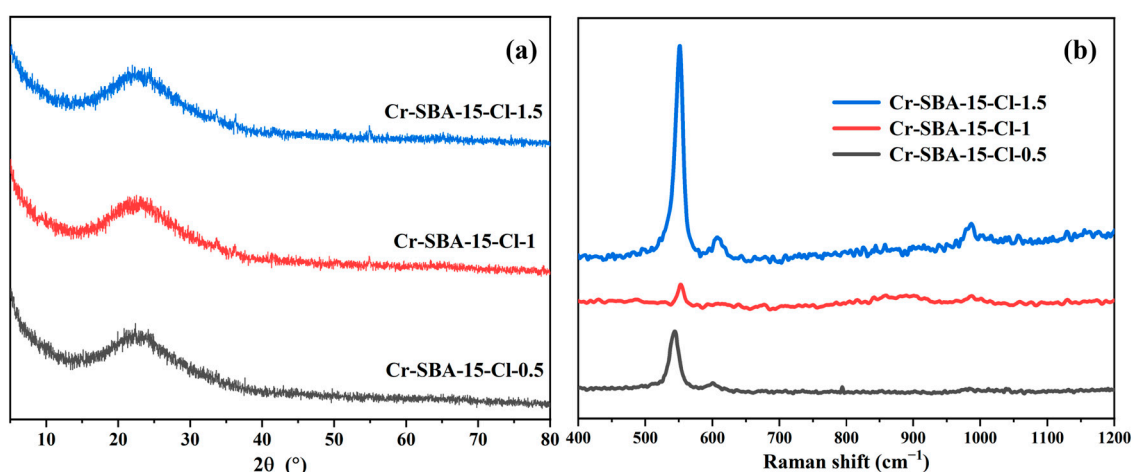


Figure 10. Dispersion of Cr on SBA-15 prepared at different pH values: (a) XRD patterns, (b) Raman spectra.

In the Raman spectra shown in Figure 10b, the peak at 550 cm^{−1} corresponds to the vibration of Cr-O bonds in Cr₂O₃. It was observed that Cr-SBA-15-Cl-1 exhibited the

smallest peak area, whereas Cr-SBA-15-Cl-1.5 showed the largest, with Cr-SBA-15-Cl-0.5 falling in between. As shown in Figure 10a, diffraction peaks characteristic of Cr_2O_3 were detected in the XRD pattern of Cr-SBA-15-Cl-1.5, but were absent in those of Cr-SBA-15-Cl-1 and Cr-SBA-15-Cl-0.5. This indicates that Cr dispersion was poorest on the surface of Cr-SBA-15-Cl-1.5, which can be attributed to the inferior mesoporous ordering of the SBA-15-Cl-1.5 support. These results demonstrate that varying the pH during SBA-15 preparation significantly impacts the support properties and the dispersion of loaded Cr. The SBA-15 support synthesized at pH 1 exhibited the optimal characteristics. This is because at pH 1, the rates of the TEOS hydrolysis–silica condensation process and the inorganic–organic self-assembly process are best matched, resulting in SBA-15 particles with superior structural regularity and the largest specific surface area.

2.3. Effect of Mixed Acids on Support Properties and DFM Performance

SBA-15 was prepared using mixed acid solutions composed of HCl mixed with H_2SO_4 , H_3PO_4 , and HNO_3 , respectively, while maintaining the pH at 1. The small-angle XRD patterns of the four supports, including SBA-15-Cl-1, are shown in Figure 11a. Upon using mixed acids, the (100), (110), and (200) diffraction peaks for all four supports remained clearly visible, with no significant changes observed in peak intensity or position.

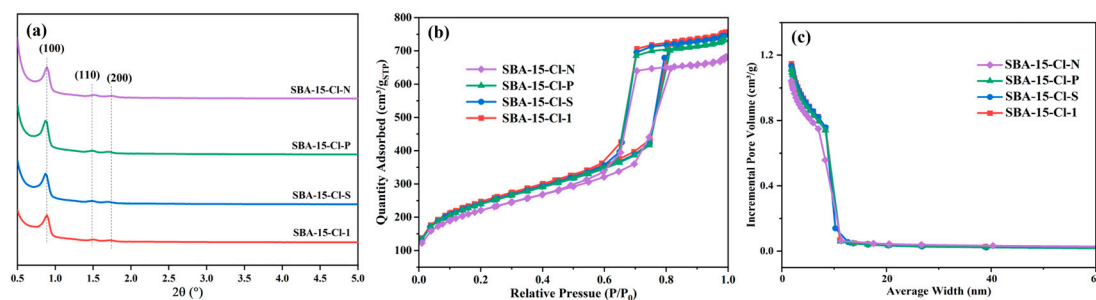


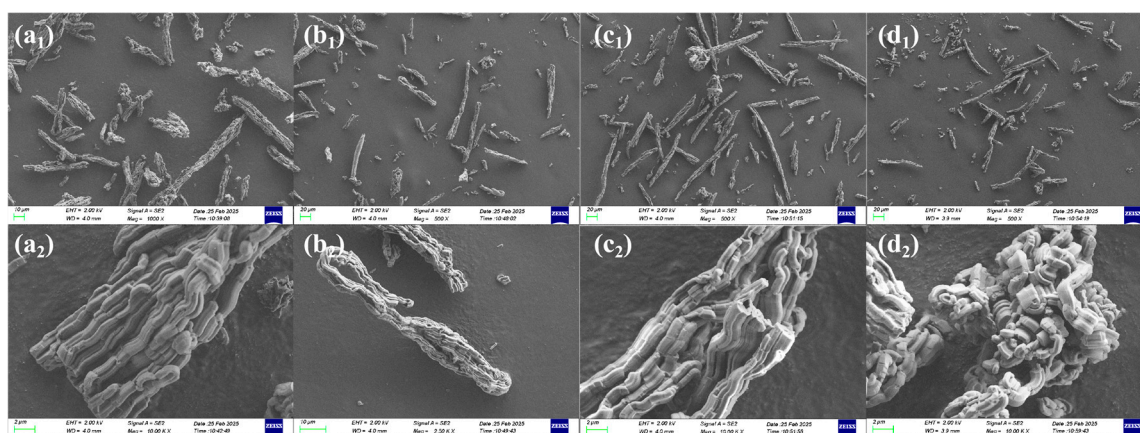
Figure 11. Structural characterization of SBA-15 supports prepared with mixed acid systems: (a) Small-angle XRD patterns, (b) N_2 adsorption–desorption isotherms, and (c) pore size distribution curves.

Figure 11b displays the N_2 adsorption–desorption isotherms of the supports. It can be observed that all four supports exhibited Type IV isotherms with H1 hysteresis loops, indicating that they all possessed standard mesoporous structures. The adsorption–desorption isotherms of SBA-15-Cl-1, SBA-15-Cl-S, and SBA-15-Cl-P nearly overlapped, suggesting minimal differences in their pore structures, which is further confirmed by the pore size distribution curves in Figure 11c. As shown in Table 5, the specific surface areas of SBA-15-Cl-1, SBA-15-Cl-S, and SBA-15-Cl-P were similar, at $887.356 \text{ m}^2/\text{g}$, $833.136 \text{ m}^2/\text{g}$, and $828.696 \text{ m}^2/\text{g}$, respectively. In contrast, SBA-15-Cl-N exhibited the smallest specific surface area ($764.196 \text{ m}^2/\text{g}$) and the smallest pore volume ($1.059 \text{ cm}^3/\text{g}$). This is because when HNO_3 is used to prepare SBA-15, it decomposes during the hydrothermal crystallization process, leading to a decrease in the concentration of NO_3^- in the solution and resulting in an actual pH greater than 1. The reduction in the number of NO_3^- ions, which act as bridging agents, weakens the interaction force between the protonated silica and the template, thereby diminishing the structural guiding role of the template. Furthermore, the decrease in H^+ concentration slows down the hydrolysis rate of tetraethyl orthosilicate (TEOS), making the silica prone to agglomeration, which results in shrinkage of the SBA-15 framework and a consequent reduction in specific surface area and pore volume.

Table 5. Textural properties of SBA-15 supports prepared using mixed acid systems.

Support	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
SBA-15-Cl-1	887.356	1.174	5.292
SBA-15-Cl-S	833.136	1.158	5.558
SBA-15-Cl-P	828.696	1.137	5.489
SBA-15-Cl-N	764.196	1.059	5.544

The particle morphologies of the four supports are illustrated in Figure 12. The particles of all four supports appeared as rope-like short rods of varying sizes, formed by the parallel stacking of hexagonal prismatic strips. On the surface of SBA-15-Cl-N particles, curved and fractured strips were observed, indicating that SBA-15-Cl-N possessed the poorest long-range structural ordering, which verifies the impact of HNO₃ decomposition on the self-assembly process. The results in Figure 2 demonstrated that SBA-15 prepared using H₃PO₄ or HNO₃ alone primarily exhibited spherical agglomerated morphologies. However, after the introduction of HCl to form a mixed acid system, the long-range ordering of the resulting SBA-15 particles was significantly improved, presenting a typical rope-like structure. This comparison suggests that the presence of Cl[−] facilitates the formation of ordered rope-like morphologies in mesoporous materials. This is attributed to the small ionic radius and single unit of negative charge of Cl[−] in the solution. When acting as a bridge, the electrostatic attraction between Cl[−] and the protonated silica is relatively weak, resulting in low interfacial bending energy, which consequently reduces the curvature of the particles.

**Figure 12.** SEM images of the supports: (a₁,a₂) SBA-15-Cl-1; (b₁,b₂) SBA-15-Cl-S; (c₁,c₂) SBA-15-Cl-P; and (d₁,d₂) SBA-15-Cl-N.

The isothermal integrated capture and conversion performance of the dual-functional materials (DFMs) composed of the four catalysts is shown in Figure 13. CaO/Cr-SBA-15-Cl-S maintained the highest ethane conversion across all three cycles, reaching 64%, 44.98%, and 38.81%, respectively. Additionally, CaO/Cr-SBA-15-Cl-S achieved the highest ethylene yield in the second and third cycles, at 33.95% and 31.74%, respectively, although its ethylene selectivity in the first cycle was only 45.91%. Conversely, CaO/Cr-SBA-15-Cl-N exhibited the lowest ethane conversion and ethylene yield. The performance of the DFMs is correlated with the dispersion of Cr on the support surface.

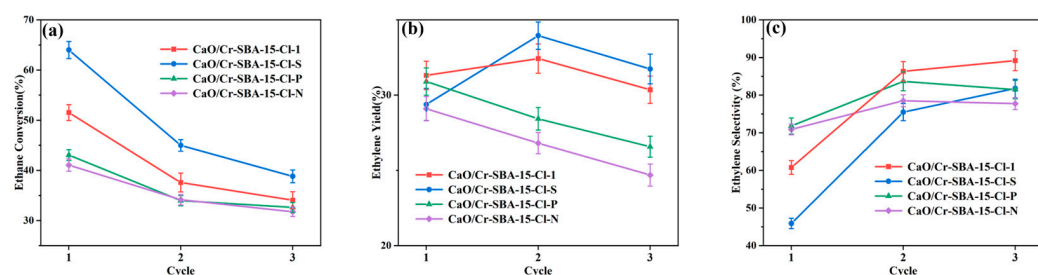


Figure 13. Cyclic catalytic performance of CaO/Cr-SBA-15-Cl-Z DFMs prepared with mixed acid systems: (a) Ethane conversion, (b) Ethylene yield, and (c) Ethylene selectivity (Capture: 700 °C, 15 vol.% CO₂, 30 mL/min, 30 min; Conversion: 700 °C, 4 vol.% C₂H₆, 30 mL/min, 30 min).

Figure 14a shows that no diffraction peaks corresponding to Cr₂O₃ were detected in the XRD patterns of the four catalysts, indicating good dispersion of Cr on these supports. Figure 14b displays the Raman spectra of the catalysts. It can be observed that the intensity of the peak at 550 cm⁻¹, which represents the content of crystalline Cr₂O₃, followed the order: Cr-SBA-15-Cl-N > Cr-SBA-15-Cl-P > Cr-SBA-15-Cl-S > Cr-SBA-15-Cl-1. This indicates that Cr dispersion was the poorest on SBA-15-Cl-N and the highest on SBA-15-Cl-1. The specific surface areas of the four supports also followed the order: SBA-15-Cl-1 > SBA-15-Cl-S > SBA-15-Cl-P > SBA-15-Cl-N. A larger specific surface area is generally more favorable for Cr dispersion.

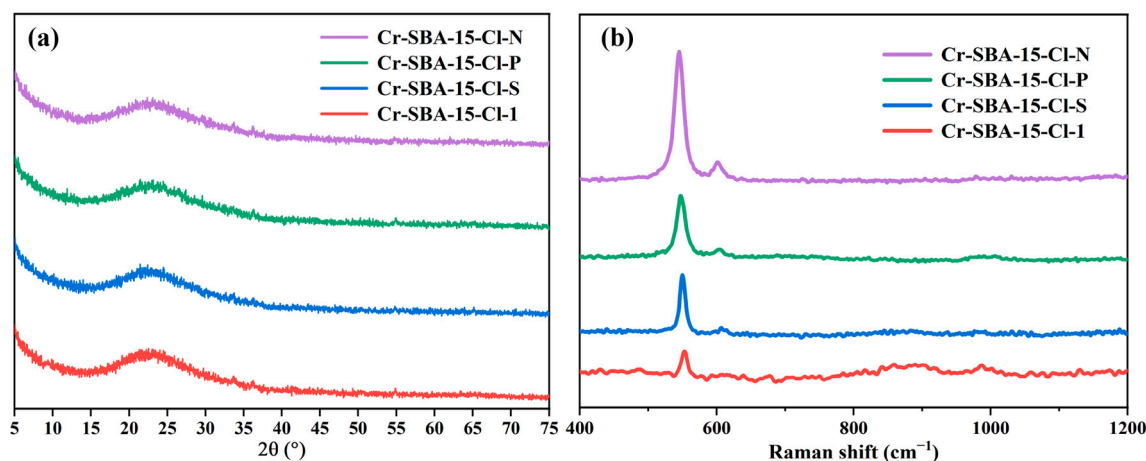


Figure 14. Comparison of Cr dispersion on SBA-15 prepared with mixed acids: (a) XRD patterns, (b) Raman spectra.

Although CaO/Cr-SBA-15-Cl-S exhibited the highest initial ethane conversion, the dispersion of Cr on its surface was lower than that on CaO/Cr-SBA-15-Cl-1. The ICP results in Table 6 show that Cr-SBA-15-Cl-S contained 0.1982 wt.% of S. This suggests that residual SO₄²⁻ enhanced the acidity of the Cr-SBA-15-Cl-S support, thereby promoting ethane activation. However, its lowest selectivity in the first two cycles indicates that increased support acidity also promotes side reactions. The high ethylene selectivity of CaO/Cr-SBA-15-Cl-1 is attributed to the superior dispersion of Cr on Cr-SBA-15-Cl-1, where isolated coordinatively unsaturated Cr³⁺ species are more inclined to catalyze ethane dehydrogenation. In contrast, Cr-SBA-15-Cl-N had the poorest Cr dispersion, and agglomerated Cr₂O₃ exhibits very low activity for oxidative dehydrogenation of ethane, resulting in the lowest ethane conversion and ethylene yield for the CaO/Cr-SBA-15-Cl-N DFM. These results demonstrate that SBA-15 prepared using mixed acids possesses good mesoporous ordering and can mitigate the influence of single acids on particle morphology and pore structure. Notably, SBA-15 prepared with the H₂SO₄-HCl mixed acid not only

possesses a favorable pore structure that facilitates Cr dispersion but also introduces S to enhance support acidity, which promotes ethane activation and thereby improves DFM performance.

Table 6. Chemical composition of the catalysts determined by ICP-OES.

Catalysts	Cr ₂ O ₃ (wt.%)	P (wt.%)	S (wt.%)
Cr-SBA-15-Cl-S	2.821	—	0.1982
Cr-SBA-15-Cl-P	2.874	0.0362	—

The long-term cyclic performance of CaO/Cr-SBA-15-Cl-S was evaluated by testing the ethane conversion, ethylene selectivity, and ethylene yield of the dual-functional material over 20 cycles, as illustrated in Figure 15a. As the number of cycles increased, both ethane conversion and ethylene yield declined rapidly during the initial five cycles, after which they stabilized at approximately 30%. Similarly, ethylene selectivity fluctuated significantly in the first five cycles before stabilizing at around 80%. The CaO/Cr-SBA-15-Cl-S DFM achieved a maximum ethylene yield of 33.30%, which stabilized at 23.61% after 20 cycles. Raman spectroscopy was employed to investigate the causes of performance degradation in the dual-functional material. The Raman spectrum of the material after 20 cycles is presented in Figure 15b. A high-intensity peak appeared at 1086.62 cm^{−1}, corresponding to the vibration of the C–O bond in CaCO₃ [43]. This indicates that with the prolongation of reaction time, the CaO sorbent within the dual-functional material gradually sintered, making the complete decomposition of CaCO₃ difficult. The peaks observed at 1350.87 cm^{−1} and 1600.86 cm^{−1} are attributed to the D-band and G-band vibrations, respectively, representing coke deposition on the surface of the dual-functional material [6]. This confirms that the primary reason for the performance degradation was the gradual coverage of active sites by coke generated from side reactions.

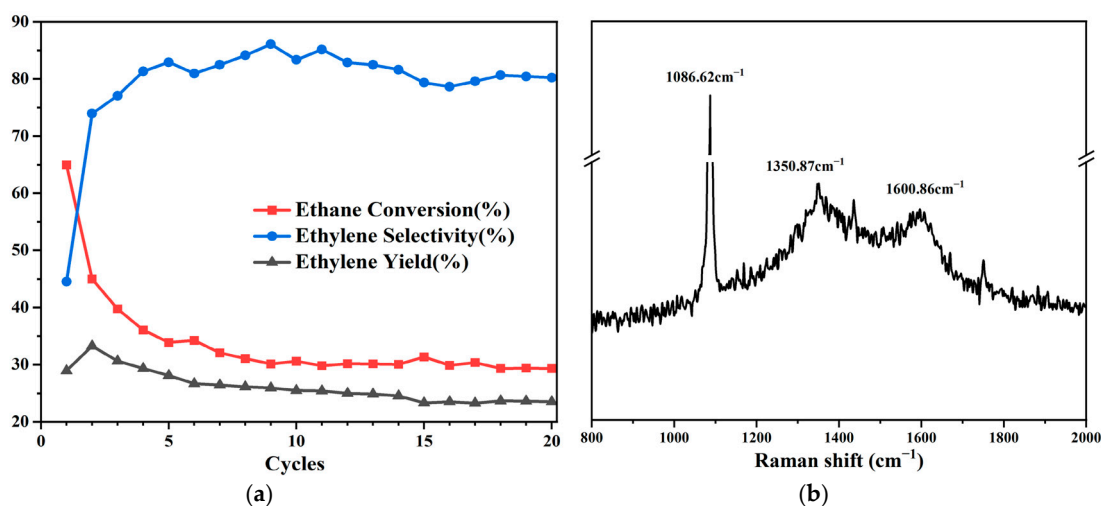


Figure 15. Analysis of long-term cyclic stability and deactivation mechanism of the optimized CaO/Cr-SBA-15-Cl-S DFM: (a) Results of 20 adsorption-dehydrogenation cycles (Capture: 700 °C, 15 vol.% CO₂, 30 mL/min, 30 min; Conversion: 700 °C, 4 vol.% C₂H₆, 30 mL/min, 30 min), (b) Raman spectrum of the sample after reaction.

To provide a more objective assessment of the advantages of the proposed CaO/Cr-SBA-15-Cl-S DFMs, their catalytic performance was compared with that of previously reported Cr-based systems using alternative supports, such as γ -Al₂O₃, SiO₂, and various zeolites, as summarized in Table 7.

Table 7. Comparison of the catalytic performance of CaO/Cr-SBA-15-Cl-S with other reported Cr-based catalysts for CO₂-ODHE or ICCU-ODHE processes.

Catalyst	Support	Ethane Conv. (%)	Ethylene Sel. (%)	Ethylene Yield (%)	Ref.
CaO/Cr-SBA-15-Cl-S	Acid-tuned SBA-15	55.62	61.04	33.95	This work
Zr-Cr/SiO ₂	SiO ₂	54.8	51.2	28.1	[44]
Zr-CrO _x /Al ₂ O ₃	γ-Al ₂ O ₃	45.3	64.1	29.0	[17]
Cr/MWW	MWW Zeolite	33.1	70.8	23.4	[19]

It can be observed that the CaO/Cr-SBA-15-Cl-S sample developed in this work exhibits superior ethane conversion and ethylene selectivity compared to many traditional supported catalysts under similar reaction conditions. Specifically, while γ-Al₂O₃-supported catalysts often suffer from strong metal-support interactions that lead to the formation of inactive Cr-Al spinel phases, the acid-controlled SBA-15 support in this study provides a more favorable environment for the high dispersion of Cr⁶⁺ active species. Furthermore, the ordered mesoporous structure and optimized surface silanol density of the CaO/Cr-SBA-15-Cl-S sample facilitate the mass transfer of reactants and products, effectively suppressing over-oxidation. This comparison demonstrates that the acid-tuning strategy for SBA-15 synthesis significantly enhances the competitive position of CaO/Cr-SBA-15 among known catalytic systems for integrated CO₂ capture and utilization.

3. Materials and Methods

3.1. Sample Preparation

The SBA-15 support in this study was synthesized following the method described in Reference [23]. SBA-15 supports prepared using four different acids (HCl, H₂SO₄, H₃PO₄, and HNO₃) were designated as SBA-15-X (where X = Cl, S, P, and N, respectively). Specifically, the corresponding acid was added dropwise into 130 mL of water until the pH reached 0.5. Subsequently, 4.0 g of P123 (EO₂₀PO₇₀EO₂₀, AR) was dissolved in the solvent until a homogeneous pale blue solution was formed. Then, 8.5 g of tetraethyl orthosilicate (TEOS, Si(OEt)₄, AR) was slowly added dropwise to the solution with continuous stirring to ensure thorough mixing. The mixture was transferred to a water bath at 40 °C and stirred continuously for 24 h, during which the solution gradually transformed into a milky white suspension. The suspension was then transferred to a Teflon-lined autoclave and crystallized in an oven at 100 °C for 24 h. After the reaction, the sample was cooled to room temperature, filtered, and washed with copious amounts of deionized water until the filtrate became neutral. The washed sample was dried in an oven overnight. Finally, the dried sample was transferred to a porcelain boat and calcined in a muffle furnace in an air atmosphere. The calcination program involved heating to 550 °C at 2 °C/min and holding for 6 h to completely remove the template, yielding SBA-15-X.

For catalyst preparation, a calculated amount of Cr(NO₃)₃·9H₂O, corresponding to a 3 wt.% Cr₂O₃ loading, was loaded onto SBA-15-X via the incipient wetness impregnation method. The sample was then dried in an oven at 80 °C. The dried sample was ground, placed in a porcelain boat, and calcined in a muffle furnace at 700 °C for 3 h in air (heating rate: 5 °C/min). The resulting catalyst was pelletized and sieved to obtain particles with a mesh size of 40–60. The ODHE catalysts were denoted as Cr-SBA-15-X, and the DFMs fabricated by mixing the as-prepared catalyst with CaO adsorbent (calcined from calcium gluconate at 900 °C) at an equal mass ratio were denoted as CaO/Cr-SBA-15-X.

To investigate the effect of solution pH during SBA-15 preparation, concentrated HCl was added during synthesis to adjust the solution pH to 0.5, 1, and 1.5. The resulting supports were denoted as SBA-15-Cl-Y (where Y = 0.5, 1, and 1.5). The corresponding ODHE catalysts and DFMs were prepared using the same method described above and denoted as Cr-SBA-15-Cl-Y and CaO/Cr-SBA-15-Cl-Y, respectively.

To investigate the effect of mixed acids, mixed acid solutions were prepared by combining a specific amount of concentrated HCl with concentrated H₂SO₄, H₃PO₄ (85%), or HNO₃ (65%) to obtain SBA-15-Cl-Z (where Z = S, P, and N). The molar amount of HCl was kept equal to that of H₂SO₄, H₃PO₄, or HNO₃ in the respective mixtures. The mixed acid solution was added to 130 mL of water until the pH reached 1. All other synthesis steps remained unchanged. The resulting supports, catalysts, and DFMs were denoted as SBA-15-Cl-Z, Cr-SBA-15-Cl-Z, and CaO/Cr-SBA-15-Cl-Z, respectively.

A certain amount of HCl was mixed with H₂SO₄, H₃PO₄, or HNO₃ in an equimolar ratio, respectively. SBA-15-Cl-Z (Z = S, P, N) was prepared at pH 1. The corresponding DFMs were designated as CaO/Cr-SBA-15-Cl-Z.

3.2. Performance of Isothermal Integrated CO₂ Capture and Conversion to Ethylene

As shown in Figure 16, the isothermal integrated CO₂ capture and ethylene conversion were conducted in a fixed-bed quartz reactor. A total of 200 mg of DFMs was loaded between two layers of quartz wool located in the middle of the reactor, and a K-type thermocouple was placed at the center of the fixed-bed reactor to monitor and control the reaction temperature of the sample in real time through a PID controller. The effluent gas was collected in gas bags and injected into a gas chromatograph (GC) for quantitative analysis. The gas flow rate passing through the sample was regulated by mass flow controllers (MFCs), with the total gas flow rate maintained at 30 mL/min. Prior to the isothermal ICCU-ODHE performance test, the sample was heated to 700 °C under N₂ atmosphere and calcined for 30 min to remove the adsorbed impurities. Afterwards, the reactor temperature was kept constant, and the feed gas was switched to 15 vol% CO₂ for a 30-min CO₂ capture process. Upon completion of the capture step, the gas atmosphere was changed to 4 vol% ethane for a 30-min CO₂ utilization test. The ethane conversion, ethylene selectivity, and ethylene yield in each cycle were calculated according to the following equations:

$$X_{C_2H_6} = \frac{(F_{C_2H_6})_0 - (F_{C_2H_6})}{(F_{C_2H_6})_0} \quad (1)$$

$$S_{C_2H_4} = \frac{(F_{C_2H_4})}{(F_{C_2H_6})_0 - (F_{C_2H_6})} \quad (2)$$

$$Y_{C_2H_4} = X_{C_2H_6} \times S_{C_2H_4} \quad (3)$$

where $(F_{C_2H_6})_0$ represents the ethane concentration collected from the corresponding blank control group, and $(F_{C_2H_6})_{out}$ and $(F_{C_2H_4})_{out}$ represent the collected concentrations of ethane and ethylene, respectively.

3.3. Characterization

The surface morphology and particle size of the samples were observed using a Nova (Hong Kong, China) NanoSEM 450 high-resolution scanning electron microscope (SEM). All samples were sputter-coated with gold prior to imaging to enhance electrical conductivity.

Nitrogen (N₂) adsorption–desorption isotherms were measured on a Micromeritics (Norcross, GA, USA) ASAP 2020 adsorption analyzer. Before measurement, the samples were degassed under vacuum at 120 °C for at least 6 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and pore characteristics were determined using the Barrett–Joyner–Halenda (BJH) method.

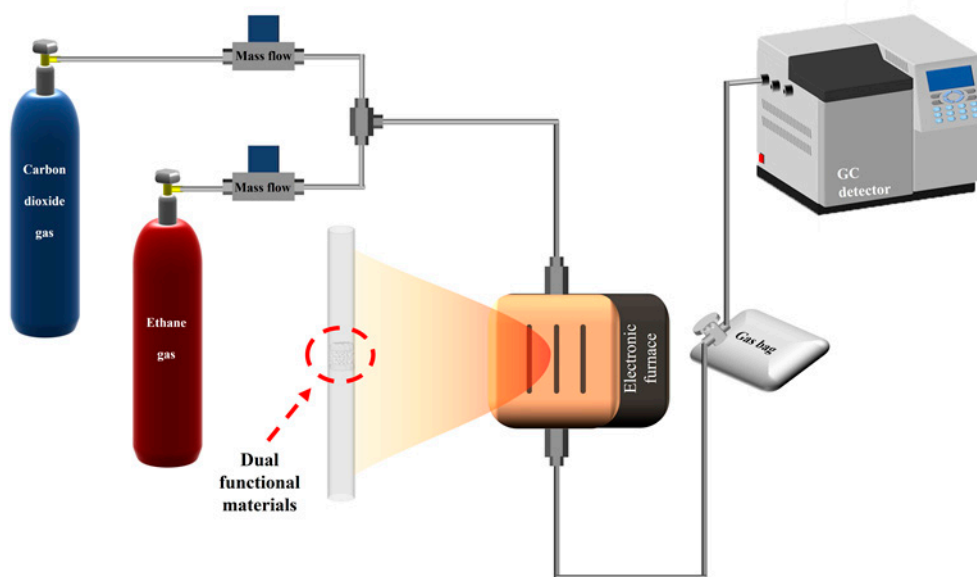


Figure 16. Schematic illustration of the experimental setup for isothermal integrated CO₂ capture-conversion to ethylene.

X-ray photoelectron spectroscopy (XPS) data were acquired using a Kratos (San Diego, CA, USA) Analytical AXIS UltraDLD system equipped with a monochromatic Al K α X-ray source (1486.6 eV) under ultra-high vacuum conditions. Survey spectra were obtained using an X-ray source operating at 7 mA/10 kV with a pass energy of 160 eV to determine the overall elemental composition. High-resolution (HR) regional spectra were recorded using a 10 mA/15 kV X-ray source with a pass energy of 20 eV, utilizing three scans to ensure the high-precision recording of characteristic peaks.

Raman spectra were obtained using a Horiba-Yvon (Palaiseau, France) Labram-HR eVolution spectrometer with an excitation laser wavelength of 532 nm and a scanning range of 400–2000 cm^{−1}.

Solid-state ²⁹Si nuclear magnetic resonance (²⁹Si NMR) spectra were recorded on a Bruker (Billerica, MA, USA) WB 400M solid-state NMR spectrometer at a spinning speed of 10 kHz, a resonance frequency of 400 MHz, an acquisition time of 0.036 milliseconds, 1600 scans, and a spectral width of 30 kHz.

The elemental content of the samples was determined using an Agilent (Santa Clara, CA, USA) 700 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). A specific mass of the sample was dissolved and cooled, and a quantitative aliquot of the solution was tested for elemental content.

X-ray diffraction (XRD) patterns were acquired using a PANalytical (Malvern, UK) X'Pert Pro diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The scanning range was 5–80° with a scanning speed of 5°/min. Small-angle X-ray scattering (SAXS) patterns for the supports were also measured on the same instrument, with a scanning range of 0.5–5° and a scanning speed of 0.5°/min.

In this study, crystallite sizes were calculated using the Scherrer equation (Equation (4)), and lattice constants were derived using Bragg's Law (Equation (5)) and the lattice constant formula for a cubic crystal system (Equation (6)).

$$D = \frac{0.9 \times \lambda}{\beta \cos \theta} \quad (4)$$

$$n\lambda = 2d_{hkl} \sin \theta \quad (5)$$

$$a = \frac{d_{hkl}}{\sqrt{h^2 + k^2 + l^2}} \quad (6)$$

where D is the crystallite size (nm), λ is the radiation wavelength (1.5406 Å), β is the full width at half maximum (FWHM) of the diffraction peak, θ is the Bragg angle corresponding to the diffraction peak, n is the diffraction order, h , k , and l are the Miller indices of the crystal plane, d_{hkl} is the interplanar spacing, and a is the lattice constant.

4. Conclusions

On the basis of the acid-dependent characteristics during SBA-15 synthesis, this study attempted to enhance the integrated CO₂ capture-conversion performance for ethylene production over CaO/Cr-SBA-15 DFMs by varying the acid type, pH value, and mixed acid ratio during SBA-15 preparation. The results demonstrated that tuning the acid environment could effectively regulate the mesoporous order, particle morphology, and surface silanol distribution of the support, thereby determining the dispersion state and oxidation valence of the active Cr species and ultimately significantly improving the ethylene production efficiency of the DFMs. Specifically, the strong acid environments provided by HCl and H₂SO₄ were more favorable for the formation of long-range ordered rope-like mesoporous structures compared with H₃PO₄ or HNO₃. The H₂SO₄ system increased the density of Cr⁶⁺ sites by optimizing the support structure, achieving the highest ethane conversion. In contrast, the HCl system directed the reaction pathway toward selective dehydrogenation via moderate surface acidity, thus yielding the highest ethylene selectivity.

Further investigation revealed that pH 1 was the optimal synthesis condition for SBA-15. Under this condition, the support exhibited the best mesoporous order and the largest specific surface area, providing an ideal anchoring environment for Cr and maximizing its dispersion. This favored the adsorption of more ethane molecules and promoted the oxidative dehydrogenation reaction.

To break the performance trade-off of single-acid systems, a mixed-acid preparation strategy was proposed in this study. The CaO/Cr-SBA-15-Cl-S DFM prepared with the HCl-H₂SO₄ mixture achieved the highest ethylene yield of 33.95%. This was attributed to the fact that the introduction of Cl[−] effectively preserved the well-ordered, rope-like morphology and pore structure of the support, while the residual SO₄^{2−} moderately enhanced the surface acidity of the support, further promoting ethane activation. Long-cycle tests indicated that the material possessed good stability, with the ethylene yield remaining stable at approximately 23.61% after five cycles. The performance decay was mainly attributed to the coverage of active sites by carbon deposits formed during the reaction and to the partial sintering of the CaO adsorbent at high temperatures, rather than to the collapse of the support framework.

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References

- Wang, Y.; Hu, P.; Yang, J.; Zhu, Y.A.; Chen, D. C–H bond activation in light alkanes: A theoretical perspective. *Chem. Soc. Rev.* **2021**, *50*, 4299–4358. [[CrossRef](#)]
- Sattler, J.J.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B.M. Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* **2014**, *114*, 10613–10653. [[CrossRef](#)] [[PubMed](#)]
- Otroshchenko, T.; Jiang, G.; Kondratenko, V.A.; Rodemerck, U.; Kondratenko, E.V. Current status and perspectives in oxidative, non-oxidative and CO₂-mediated dehydrogenation of propane and isobutane over metal oxide catalysts. *Chem. Soc. Rev.* **2021**, *50*, 473–527. [[CrossRef](#)]
- Gambo, Y.; Adamu, S.; Tanimu, G.; Abdullahi, I.M.; Lucky, R.A.; Ba-Shammakh, M.S.; Hossain, M.M. CO₂-mediated oxidative dehydrogenation of light alkanes to olefins: Advances and perspectives in catalyst design and process improvement. *Appl. Catal. A Gen.* **2021**, *623*, 118273. [[CrossRef](#)]
- Baamran, K.; Lawson, S.; Rezaei, F.; Rownaghi, A.A. Reactive carbon capture: Cooperative and bifunctional Adsorbent-Catalyst materials and process integration for a new carbon economy. *Acc. Chem. Res.* **2024**, *57*, 2383–2394. [[CrossRef](#)]
- Du, M.; Nan, B.; Li, Y.; Liu, Z.; Hou, K.; Qin, Y.; Zheng, G.; Liang, Z.; Zhang, L.; Wang, D.-L.; et al. In situ generation of the spinel structured FeCr₂O₄ catalyst for CO₂-assisted ethane oxidative dehydrogenation. *J. Mater. Chem. A* **2025**, *13*, 36151–36165. [[CrossRef](#)]
- Zhang, X.; Wei, W.; Wang, S.; Tan, Y.; Zhao, J.; Cao, S.; Liu, W. Efficient sorbent/catalyst composites for CO₂-mediated oxidative dehydrogenation of ethane via isothermal integrated CO₂ capture and utilization. *Sep. Purif. Technol.* **2025**, *357*, 129941. [[CrossRef](#)]
- Xie, Q.; Miao, C.; Hua, W.; Yue, Y.; Gao, Z. Ga-doped MgAl₂O₄ spinel as an efficient catalyst for ethane dehydrogenation to ethylene assisted by CO₂. *Ind. Eng. Chem. Res.* **2021**, *60*, 11707–11714. [[CrossRef](#)]
- Al-Mamoori, A.; Lawson, S.; Rownaghi, A.A.; Rezaei, F. Oxidative dehydrogenation of ethane to ethylene in an integrated CO₂ capture-utilization process. *Appl. Catal. B Environ.* **2020**, *278*, 119329. [[CrossRef](#)]
- Al-Mamoori, A.; Alghamdi, T.; Rownaghi, A.A.; Rezaei, F. Enhancing the ethylene yield over hybrid adsorbent catalyst materials in CO₂-assisted oxidative dehydrogenation of ethane by tuning catalyst support properties. *Energy Fuels* **2020**, *34*, 14483–14492. [[CrossRef](#)]
- Velty, A.; Corma, A. Advanced zeolite and ordered mesoporous silica-based catalysts for the conversion of CO₂ to chemicals and fuels. *Chem. Soc. Rev.* **2023**, *52*, 1773–1946. [[CrossRef](#)] [[PubMed](#)]
- Lawson, S.; Baamran, K.; Newport, K.; Rezaei, F.; Rownaghi, A.A. Formulation and processing of dual functional Adsorbent/Catalyst structured monoliths using an additively manufactured contactor for direct Capture/Conversion of CO₂ with cogeneration of ethylene. *Chem. Eng. J.* **2022**, *431*, 133224. [[CrossRef](#)]
- Baamran, K.; Lawson, S.; Rownaghi, A.A.; Rezaei, F. Process evaluation and kinetic analysis of 3D-printed monoliths comprised of CaO and Cr/H-ZSM-5 in combined CO₂ Capture-C₂H₆ oxidative dehydrogenation to C₂H₄. *Chem. Eng. J.* **2022**, *435*, 134706. [[CrossRef](#)]
- Zhang, X.; Wei, W.; Ma, J.; Zhang, T.; Wang, Y.; Sun, H.; Wang, F.; Liu, W. Assessment of CaO-based sorbent/spinel catalyst composites for the oxidative dehydrogenation of ethane in isothermal integrated CO₂ capture and utilization. *Sep. Purif. Technol.* **2024**, *328*, 124924. [[CrossRef](#)]
- Zhang, X.; Liu, W.; Peng, P.; Zhang, Z.; Du, Q.; Shi, J.; Deng, L. A dual functional sorbent/catalyst material for in-situ CO₂ capture and conversion to ethylene production. *Fuel* **2023**, *351*, 128701. [[CrossRef](#)]
- de Oliveira, J.F.; Volanti, D.P.; Bueno, J.M.; Ferreira, A.P. Effect of CO₂ in the oxidative dehydrogenation reaction of propane over Cr/ZrO₂ catalysts. *Appl. Catal. A Gen.* **2018**, *558*, 55–66. [[CrossRef](#)]
- Wei, S.; Wang, C.; Zhou, L.; Zhang, X.; Zhou, Z.; Liu, X. Zr-modified γ -Al₂O₃ supported CrO_x catalyst for CO₂ assisted ethane dehydrogenation. *Fuel* **2025**, *382*, 133770. [[CrossRef](#)]
- Al-Awadi, A.S.; El-Toni, A.M.; Labis, J.P.; Khan, A.; Ghaitan, H.; Al-Zahrani, A.A.; Abasaeed, A.E.; Al-Zahrani, S.M. Mesoporous organo-silica supported chromium oxide catalyst for oxidative dehydrogenation of ethane to ethylene with CO₂. *Catalysts* **2021**, *11*, 642. [[CrossRef](#)]
- Wan, T.; Jin, F.; Cheng, X.; Gong, J.; Wang, C.; Wu, G.; Liu, A. Influence of hydrophilicity and titanium species on activity and stability of Cr/MWW zeolite catalysts for dehydrogenation of ethane with CO₂. *Appl. Catal. A Gen.* **2022**, *637*, 118542. [[CrossRef](#)]

20. Cheng, Y.; Miao, C.; Hua, W.; Yue, Y.; Gao, Z. Cr/ZSM-5 for ethane dehydrogenation: Enhanced catalytic activity through surface silanol. *Appl. Catal. A Gen.* **2017**, *532*, 111–119. [\[CrossRef\]](#)
21. Miao, C.; Chen, S.; Liang, L.; Shang, K.; Ouyang, J. Construction of flower spherical Cr–Ce/ZSM-5 catalyst with rich surface structure and study on CO₂-assisted ethane dehydrogenation performance. *Microporous Mesoporous Mater.* **2023**, *348*, 112392. [\[CrossRef\]](#)
22. Wang, J.; Zhu, M.L.; Song, Y.H.; Liu, Z.T.; Wang, L.; Liu, Z.W. Molecular-level investigation on supported CrO_x catalyst for oxidative dehydrogenation of propane with carbon dioxide. *J. Catal.* **2022**, *409*, 87–97. [\[CrossRef\]](#)
23. Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G.H.; Chmelka, B.F.; Stucky, G.D. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science* **1998**, *279*, 548–552. [\[CrossRef\]](#) [\[PubMed\]](#)
24. El Eter, M.; Hamzaoui, B.; Abou-Hamad, E.; Pelletier, J.D.A.; Basset, J.-M. Well-defined azazirconacyclopropane complexes supported on silica structurally determined by 2D NMR comparative elucidation. *Chem. Commun.* **2013**, *49*, 4616–4618. [\[CrossRef\]](#)
25. Wei, S.; Dai, H.; Long, J.; Lin, H.; Gu, J.; Zong, X.; Yang, D.; Tang, Y.; Yang, Y.; Dai, Y. Nonoxidative propane dehydrogenation by isolated Co²⁺ in BEA zeolite: Dealumination-determined key steps of propane CH activation and propylene desorption. *Chem. Eng. J.* **2023**, *455*, 140726. [\[CrossRef\]](#)
26. Ide, M.; El-Roz, M.; De Canck, E.; Vicente, A.; Planckaert, T.; Bogaerts, T.; Van Driessche, I.; Lynen, F.; Van Speybroeck, V.; Thybault-Starzyk, F.; et al. Quantification of silanol sites for the most common mesoporous ordered silicas and organosilicas: Total versus accessible silanols. *Phys. Chem. Chem. Phys.* **2013**, *15*, 642–650. [\[CrossRef\]](#)
27. Xian, Q.; He, X.; Chen, L.; Wang, E.; Dan, H.; Ding, Y. Controllable synthesis of mesoporous SBA-15 using H₂SO₄. *Philos. Mag. Lett.* **2021**, *101*, 203–210. [\[CrossRef\]](#)
28. Pinto, F.G.H.S.; Caldeira, V.P.D.S.; Villarroel-Rocha, J.; Sapag, K.; Pergher, S.B.C.; Santos, A.G.D. Al/SBA-15 mesoporous material: A study of pH influence over aluminum insertion into the framework. *Nanomaterials* **2024**, *14*, 208. [\[CrossRef\]](#)
29. Zhao, D.; Yang, P.; Chmelka, B.F.; Stucky, G.D. Multiphase assembly of mesoporous–macroporous membranes. *Chem. Mater.* **1999**, *11*, 1174–1178. [\[CrossRef\]](#)
30. Kruk, M.; Cao, L. Pore size tailoring in large-pore SBA-15 silica synthesized in the presence of hexane. *Langmuir* **2007**, *23*, 7247–7254. [\[CrossRef\]](#)
31. Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B.F.; Stucky, G.D. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. *J. Am. Chem. Soc.* **1998**, *120*, 6024–6036. [\[CrossRef\]](#)
32. ShengáSu, D. Alkanes-assisted low temperature formation of highly ordered SBA-15 with large cylindrical mesopores. *Chem. Commun.* **2005**, *42*, 5343–5345. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Iga, G.D.; Vieira, J.L.; Santos, É.A.; Albuquerque, J.S.; Urquieta-González, E.A.; Bueno, J.M.C.; Gallo, J.M.R. Should we still be using HCl in the synthesis of SBA-15 and Al-SBA-15? *Microporous Mesoporous Mater.* **2024**, *378*, 113222. [\[CrossRef\]](#)
34. Echeverría, J.C.; Moriones, P.; Arzamendi, G.; Garrido, J.J.; Gil, M.J.; Cornejo, A.; Martínez-Merino, V. Kinetics of the acid-catalyzed hydrolysis of tetraethoxysilane (TEOS) by ²⁹Si NMR spectroscopy and mathematical modeling. *J. Sol-Gel Sci. Technol.* **2018**, *86*, 316–328. [\[CrossRef\]](#)
35. Silva, F.E.D.; Rigoti, E.; Mello, M.I.S.D.; Pergher, S.B. Tuning textural properties by changing the morphology of SBA-15 mesoporous materials. *Materials* **2024**, *17*, 2827. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Muñoz, M.; Flores, D.; Morillo, G.; Narváez, R.; Marcilla, A.; Rosero, M. Comprehensive Review of SBA-15 Mesoporous Silica: Functionalization Strategies, Diffusion Mechanisms, and Emerging Applications. *Sustain. Chem.* **2025**, *6*, 42. [\[CrossRef\]](#)
37. Osipov, A.A.; Liška, M.; Osipova, L.M.; Chromčíková, M.; Hruška, B. Thermodynamic modeling and Raman spectroscopy study of Na₂O–TiO₂–SiO₂ glasses. *Vib. Spectrosc.* **2020**, *111*, 103160. [\[CrossRef\]](#)
38. Xu, S. The capacity fading mechanism of high-capacity CrO_x (x ≥ 2.5) cathode material for lithium-ion battery. *J. Appl. Electrochem.* **2024**, *54*, 1957–1968. [\[CrossRef\]](#)
39. Joo, S.Y.; Loka, C.; Jo, Y.W.; Reddyprakash, M.; Moon, S.W.; Choi, Y.; Lee, S.E.; Cho, G.S.; Lee, K.S. ITO/SiO₂/ITO structure on a sapphire substrate using the oxidation of ultra-thin Si films as an insulating layer for one-glass-solution capacitive touch-screen panels. *Coatings* **2020**, *10*, 134. [\[CrossRef\]](#)
40. Ivanova, T.M.; Maslakov, K.I.; Linko, R.V.; Evstifeev, I.S.; Kiskin, M.A.; Shcherbakov, I.N.; Savilov, S.V.; Lunin, V.V.; Novotortsev, V.M.; Eremenko, I.L. XPS study of the electronic structure of heterometallic complexes [Fe₂MO(O₂CCH₃)₆(H₂O)₃]₃H₂O (M = Co, Ni). *Russ. J. Inorg. Chem.* **2014**, *59*, 670–677. [\[CrossRef\]](#)
41. Alawi, M.A.; Hasan, L.A.; Tanaka, K. Improved photocatalytic degradation of insecticide pirimicarb on SiO₂-LOADED TiO₂. *Fresenius Environ. Bull.* **2007**, *16*, 403.
42. Huang, Y.; Ma, L.; Huang, Z.; Lai, W.; Zheng, Y.; Xu, M.; Yang, A.; Liang, L.; Lu, Z.; Zhou, J.; et al. Effect of stearic acid and sodium stearate on hydrophobicity of nano calcium carbonate and mechanism of water vapor adsorption. *Sci. Rep.* **2025**, *15*, 364. [\[CrossRef\]](#) [\[PubMed\]](#)

43. Colombo, R.; Moroni, G.; Negri, C.; Delen, G.; Monai, M.; Donazzi, A.; Weckhuysen, B.M.; Maestri, M. Surface Carbon Formation and its Impact on Methane Dry Reforming Kinetics on Rhodium-Based Catalysts by Operando Raman Spectroscopy. *Angew. Chem. Int. Ed.* **2024**, *63*, e202408668. [[CrossRef](#)] [[PubMed](#)]
44. Li, X.; Liu, S.; Chen, H.; Luo, S.-Z.; Jing, F.; Chu, W. Improved catalytic performance of ethane dehydrogenation in the presence of CO₂ over Zr-promoted Cr/SiO₂. *ACS Omega* **2019**, *4*, 22562–22573. [[CrossRef](#)] [[PubMed](#)]

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