

## Article

# Designing a Cr<sup>3+</sup>-Based Transition Metal Catalyst: Redox-Mediated Low-Temperature Activation for Strong Solid Base Generation

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## Abstract

Solid base catalysts hold significant promise for replacing traditional homogeneous bases with green chemical processes. However, the construction of their strong basic sites typically relies on high-temperature calcination, which often leads to the collapse of the carrier structure and high energy consumption. This study proposes a novel “carrier reducibility tuning” strategy, which involves endowing the carrier with intrinsic reducibility to induce the low-temperature decomposition of alkali precursors via a redox pathway, thereby enabling the mild construction of strong basic sites. Low-valence Cr<sup>3+</sup> was doped into a mesoporous zirconia framework, successfully fabricating an MCZ carrier with a mesostructure and reducible characteristics. Characterization results indicate that a significant redox interaction between the Cr<sup>3+</sup> in the carrier and the supported KNO<sub>3</sub> occurs at 500 °C. This interaction facilitates the complete conversion of KNO<sub>3</sub> into highly dispersed, strongly basic K<sub>2</sub>O species, while Cr<sup>3+</sup> is predominantly oxidized to Cr<sup>6+</sup>. This activation temperature is approximately 300 °C lower than that required for the conventional thermal decomposition pathway and effectively preserves the structural integrity of the material. In the transesterification reaction for synthesizing dimethyl carbonate, the prepared catalyst exhibits superior catalytic activity, significantly outperforming classic solid bases like MgO and other reference catalysts.

**Keywords:** solid strong base; chromium doping; low-temperature activation; redox interaction; transesterification



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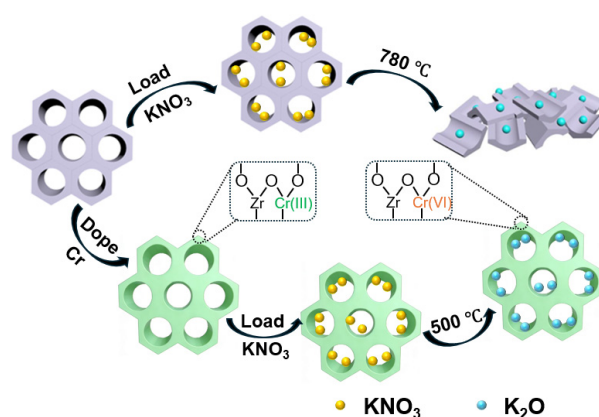
## 1. Introduction

Catalysts are indispensable in the chemical industry, with over 90% of chemical processes relying on their use. Among them, solid base catalysts represent a crucial class of heterogeneous catalytic materials, attracting significant attention for replacing traditional homogeneous bases [1–8]. They offer distinct advantages such as facile product separation, reduced equipment corrosion, and lower waste generation [9–16]. These merits make them highly promising for important reactions including transesterification, Knoevenagel condensation, and Michael addition. Substantial progress has been made in the development of solid base catalysts over the past decades [17–23]. For instance, novel catalysts have been prepared through strategies like nitrogen-doping or grafting organic basic groups onto supports [24]. However, these methods often suffer from complex procedures, high costs, and most critically, the resulting materials typically exhibit only

moderate basicity. To achieve stronger basicity, alternative approaches focus on introducing strong basic species (e.g.,  $\text{K}_2\text{O}$ ) into porous carriers. A common method involves loading alkali precursors like  $\text{KNO}_3$  onto supports such as  $\text{Al}_2\text{O}_3$  or mesoporous silica SBA-15, followed by high-temperature thermal treatment. For example, complete conversion of  $\text{KNO}_3$  to active sites requires calcination at approximately  $700^\circ\text{C}$  on  $\text{Al}_2\text{O}_3$  and around  $750^\circ\text{C}$  on SBA-15 [11,25–27].

Unfortunately, such harsh activation conditions lead to inevitable drawbacks: (1) collapse or sintering of the mesoporous support structure, causing a drastic decrease in surface area and mass transfer limitations; and (2) high energy consumption, which increases costs and hinders industrial scalability. Therefore, developing a novel strategy to construct strong basic sites under relatively mild conditions while preserving the structural integrity of the support remains a critical and unresolved challenge.

In this study, we propose an innovative “reducibility tuning” strategy. The core concept is to endow the carrier with inherent reducibility, creating a redox environment between the host (carrier) and guest (precursor). This environment is designed to promote the decomposition of the alkali precursor via a redox reaction pathway at a significantly lower temperature. The ongoing development of advanced inorganic materials for energy and chemical conversion applications underscores the importance of tailored material design in modern catalysis [28–37]. Zirconia ( $\text{ZrO}_2$ ), known for its high melting point, low thermal conductivity, and excellent corrosion resistance, serves as an attractive catalyst support [38]. We successfully constructed a reducible carrier by incorporating low-valence  $\text{Cr}^{3+}$  ions into a mesoporous zirconia framework (Scheme 1). Characterization results reveal that the introduced  $\text{Cr}^{3+}$  not only stabilizes the structure but also strongly interacts with the loaded  $\text{KNO}_3$ . This redox interaction enables the complete decomposition of  $\text{KNO}_3$  at  $500^\circ\text{C}$ , which is approximately  $300^\circ\text{C}$  lower than the temperature required by conventional thermal decomposition routes on undoped supports (e.g.,  $>780^\circ\text{C}$ ). Multiple characterization techniques confirm that during this low-temperature activation,  $\text{Cr}^{3+}$  is predominantly oxidized to  $\text{Cr}^{6+}$ , while  $\text{KNO}_3$  is reduced and transformed into highly dispersed, strongly basic  $\text{K}_2\text{O}$  species. This mechanism fundamentally differs from the traditional thermal cracking process widely reported in the literature. The resulting solid strong base catalyst possesses a series of porous structures and abundant strong basic sites. It demonstrates superior catalytic performance in the model transesterification reaction for dimethyl carbonate synthesis, outperforming classic solid bases like  $\text{MgO}$  and other reported benchmark catalysts.



**Scheme 1.** Schematic Illustration of the Contrasting  $\text{KNO}_3$  Conversion Pathways on  $\text{ZrO}_2$  versus Cr-Doped MCZ Supports.

## 2. Results and Discussion

### 2.1. Mechanism of Low-Temperature KNO<sub>3</sub> Decomposition

Understanding the activation pathway of the KNO<sub>3</sub> precursor is crucial, as it directly determines the formation temperature of strong basic sites (K<sub>2</sub>O) and the structural integrity of the support. We employed thermogravimetric analysis coupled with mass spectrometry (TG-MS) to probe the thermal decomposition process in situ, simultaneously monitoring weight loss and the evolution of gaseous products. The MS signals for characteristic fragments of NO ( $m/z = 30$ ), O<sub>2</sub> ( $m/z = 32$ ), N<sub>2</sub>O ( $m/z = 44$ ), and NO<sub>2</sub> ( $m/z = 46$ ) were tracked to elucidate the decomposition mechanism [39,40].

Figure 1a presents the TG-MS profiles for KNO<sub>3</sub> supported on undoped mesoporous zirconia (K/ZrO<sub>2</sub>). A single weight-loss step is observed, centered at approximately 780 °C. This high-temperature event corresponds to the conventional thermal cracking of KNO<sub>3</sub>. The concomitant MS signals show the primary release of NO, N<sub>2</sub>O, and O<sub>2</sub>, confirming a decomposition pathway dominated by simple thermal energy input, which inevitably risks sintering the ZrO<sub>2</sub> framework. In striking contrast, the KNO<sub>3</sub>-loaded, Cr-doped zirconia sample (KMCZ) exhibits a profoundly different profile (Figure 1b). The decomposition occurs in two distinct, sequential steps at significantly lower temperatures (350 °C and 500 °C). The drastic reduction in the onset temperature by over 300 °C unambiguously demonstrates that the presence of Cr<sup>3+</sup> ions in the zirconia lattice catalyzes the decomposition process. More importantly, the composition of the evolved gases shifts notably. While NO and N<sub>2</sub>O are still detected, the signal for O<sub>2</sub> has substantially disappeared, and a pronounced release of NO<sub>2</sub> is observed. This shift in product distribution from O<sub>2</sub> to NO<sub>2</sub> is a critical indicator of a changed chemical pathway, which is consistent with a change from a mere thermal dissociation to a redox process involving Cr<sup>3+</sup>. The distinct product profiles point to two different overall reaction stoichiometries. On the inert ZrO<sub>2</sub> support, decomposition likely follows a classic thermal dissociation path approximated by:

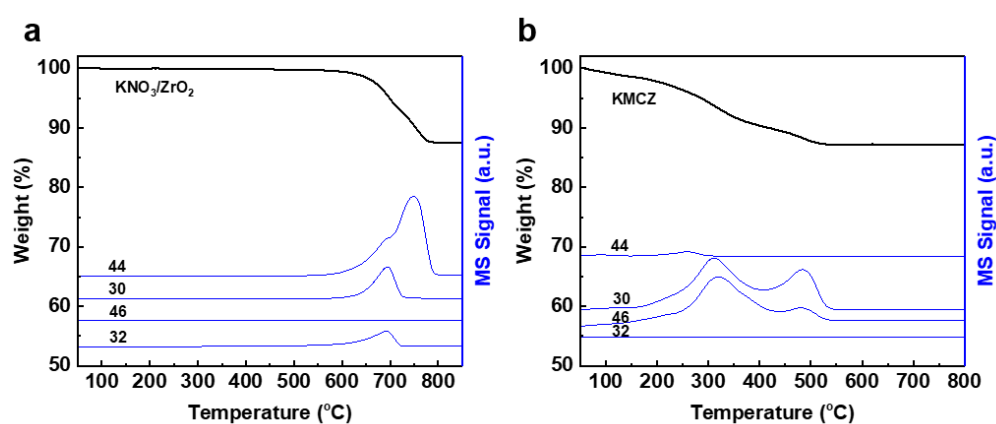
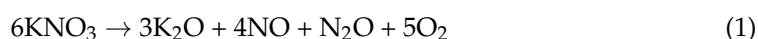
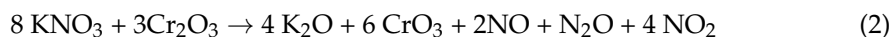


**Figure 1.** TG-MS analysis of (a) K/ZrO<sub>2</sub>, (b) KMCZ samples. The  $m/z$  value of 44, 30, 46, and 32 in MS signal corresponds to N<sub>2</sub>O, NO, NO<sub>2</sub>, and O<sub>2</sub>, respectively.

Conversely, on the reducible MCZ support, Cr<sup>3+</sup> acts as a reducing agent. We propose that KNO<sub>3</sub> (where N is in the +5-oxidation state) is reduced, leading to the formation of NO<sub>2</sub> (where N is in the +4-oxidation state), while Cr<sup>3+</sup> is simultaneously oxidized to Cr<sup>6+</sup> (likely in the form of CrO<sub>3</sub>). Based on the observed gaseous products and the oxidation state

change of Cr, a plausible redox-mediated conversion can be represented by the following balanced stoichiometry:



This stoichiometry is mass- and charge-balanced. The specific mixture of gaseous nitrogen oxides (NO, N<sub>2</sub>O, NO<sub>2</sub>) is consistent with the non-catalytic reductive decomposition pathways of nitrate and, crucially, is directly evidenced by the TG-MS profiles in Figure 1b. The significant production of NO<sub>2</sub> alongside the suppression of O<sub>2</sub> evolution is a key feature distinguishing the proposed redox pathway from the simple thermal decomposition described by Equation (1). The two-stage weight loss in KMCZ may correspond to the sequential decomposition of KNO<sub>3</sub> interacting with Cr sites of different accessibility or the stepwise formation of different intermediate species. This low-temperature, redox-driven mechanism is the cornerstone of our strategy, as it enables the generation of active K<sub>2</sub>O species while preserving the mesoporous host structure from high-temperature damage.

To monitor the crystalline phase evolution during the synthesis and activation process, XRD was performed on a series of samples, and the results are presented in Figure 2a. For the support MCZ, distinct diffraction peaks are observed at  $2\theta = 30.3^\circ$ ,  $35.3^\circ$ ,  $50.4^\circ$ , and  $60.2^\circ$ . These peaks can be indexed to the (111), (200), (220), and (311) crystal planes of tetragonal zirconia (t-ZrO<sub>2</sub>, JCPDS No. 17-0923), respectively, confirming the successful formation of a crystalline framework after calcination at 600 °C [41]. Upon loading the KNO<sub>3</sub> precursor onto the Cr-doped support (sample KMCZ), new diffraction peaks emerge at  $23.9^\circ$ ,  $29.4^\circ$ ,  $33.9^\circ$ ,  $41.1^\circ$ , and  $42.0^\circ$ . These peaks are characteristic of crystalline, orthorhombic-phase KNO<sub>3</sub> (JCPDS No. 15-0607) [42,43], indicating that the impregnation process deposited KNO<sub>3</sub> in a well-crystallized form on the MCZ surface. After activation at 300 °C under N<sub>2</sub> (sample KMCZ-300), the characteristic peaks of KNO<sub>3</sub> remain clearly visible, albeit with reduced intensity. This suggests that only a minor fraction of KNO<sub>3</sub> has decomposed at this temperature, consistent with the initial weight-loss step observed in the TG-MS analysis. For samples activated at 500 °C and 700 °C (KMCZ-500 and KMCZ-700), all diffraction peaks corresponding to crystalline KNO<sub>3</sub> completely disappear. This provides direct evidence that KNO<sub>3</sub> is fully converted on the MCZ support by 500 °C. Together, these data conclusively demonstrate that the incorporation of Cr<sup>3+</sup> drastically promotes the conversion of KNO<sub>3</sub>, lowering the required temperature by nearly 300 °C compared to its decomposition on undoped zirconia. It is interesting to note that no diffraction peaks assignable to Cr<sub>2</sub>O<sub>3</sub> were observed in all the samples. This suggests that the Cr<sup>3+</sup> ions are not aggregated into separate nanoparticles or bulk oxide crystallites on the surface. Instead, they are successfully incorporated into the zirconia lattice, likely substituting for Zr<sup>4+</sup> ions, forming a solid solution. This high dispersion and integration of Cr species within the support framework are crucial for creating the uniform redox-active sites necessary for the low-temperature, interactive decomposition of KNO<sub>3</sub>.

FT-IR spectroscopy was employed to monitor the removal of organic templates and the evolution of the nitrate precursor. As shown in Figure 2b, the spectrum of the as-synthesized material before calcination shows characteristic bands at 1640 and 1540 cm<sup>−1</sup>, attributable to amide groups from the CAPB template, and a band at 1120 cm<sup>−1</sup> from the C-O-C stretching vibration of the P123 template. After calcination at 600 °C to obtain the MCZ support, these bands completely disappear, confirming the thorough removal of the organic structure-directing agents. Concurrently, two new bands emerge at approximately 600 and 510 cm<sup>−1</sup>, which are characteristic of the tetragonal phase of zirconia [44,45]. Upon loading KNO<sub>3</sub> (sample KMCZ), a strong, sharp band appears at 1383 cm<sup>−1</sup>, which is assigned to the N–O stretching vibration of the nitrate ion (NO<sub>3</sub><sup>−</sup>) [46]. After activation at 300 °C (KMCZ-300), the intensity of this nitrate band diminishes but remains clearly

detectable, indicating the partial decomposition of  $\text{KNO}_3$  at this temperature. Crucially, upon activation at 500 °C and 700 °C (KMCZ-500 and KMCZ-700), this characteristic nitrate band vanishes entirely. This FT-IR evidence directly confirms the complete decomposition of  $\text{KNO}_3$  on the MCZ support by 500 °C, consistent with the XRD and TG-MS findings, and further reinforces the promoting role of Cr in enabling low-temperature conversion.

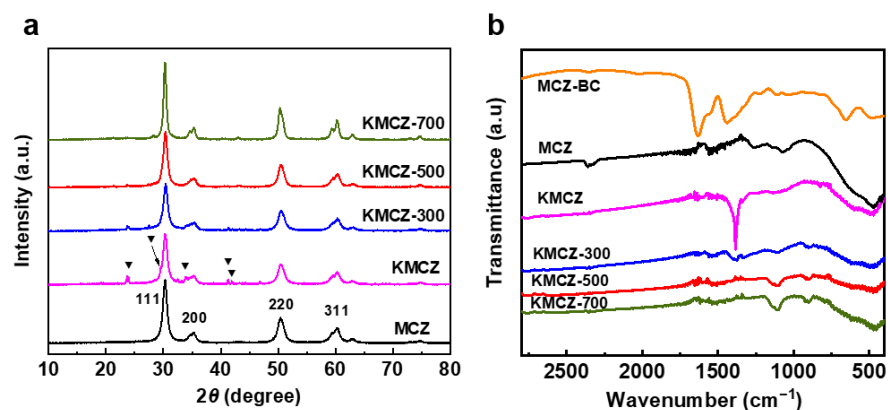


**Figure 2.** (a) Wide-angle XRD, (b) FT-IR spectra of series samples.

XPS analysis provided direct chemical-state evidence for the proposed redox mechanism. The N 1s spectra are displayed in Figure 3a. For the KMCZ precursor, a distinct peak is observed at a binding energy of 406.7 eV, which is characteristic of nitrogen in the nitrate species [47]. After activation at 500 °C (KMCZ-500), this N 1s peak completely disappears, providing definitive proof that the  $\text{KNO}_3$  precursor has been fully converted, with no residual nitrate detectable on the surface. The corresponding changes in the chemical state of chromium were tracked using the Cr 2p spectra (Figure 3b). For the KMCZ precursor, the Cr 2p<sub>3/2</sub> and Cr 2p<sub>1/2</sub> peaks are located at BEs of 576.7 eV and 587.1 eV, respectively, consistent with the presence of  $\text{Cr}^{3+}$  species [4,48]. After activation at 500 °C, the Cr 2p spectrum is dominated by new peaks at binding energies of 580.2 eV and 589.4 eV, characteristic of  $\text{Cr}^{6+}$  [49]. This significant shift of approximately 3.5 eV relative to the precursor positions, along with the drastic reduction in the original  $\text{Cr}^{3+}$  signals, provides definitive evidence for the predominant oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ . This major chemical state change of chromium, concurrent with the complete disappearance of nitrate nitrogen, offers direct spectroscopic confirmation of the redox reaction pathway expressed in Equation (2).

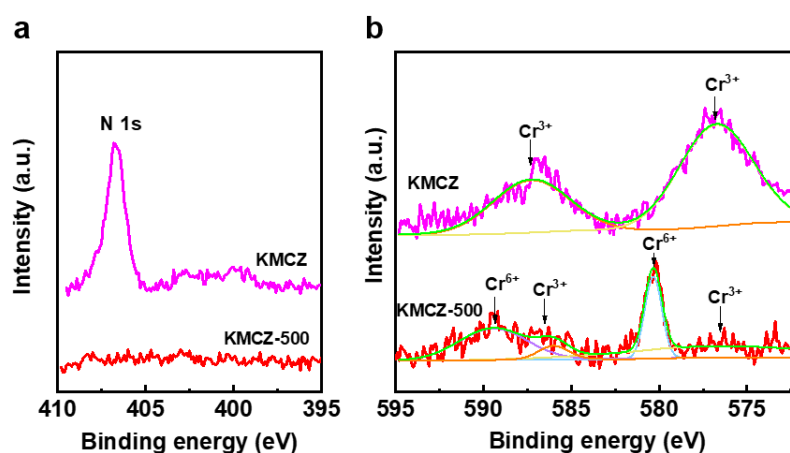


**Figure 3.** XPS spectra of different samples. (a) N 1s and (b) Cr 2p before and after calcination.

The oxidation state change of chromium is accompanied by a distinct visual color transition, as shown in the photographic images of the samples (Figure 4). The K/MCZ

precursor exhibits a dark yellowish-brown color, typical of  $\text{Cr}^{3+}$ -containing compounds. As the activation temperature increases, the color of the catalysts progressively lightens. Samples activated at 500 °C and above turn into a light-yellow hue, which is characteristic of  $\text{Cr}^{6+}$  species. This macroscopic color change provides intuitive, supporting evidence for the oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  during the activation process.

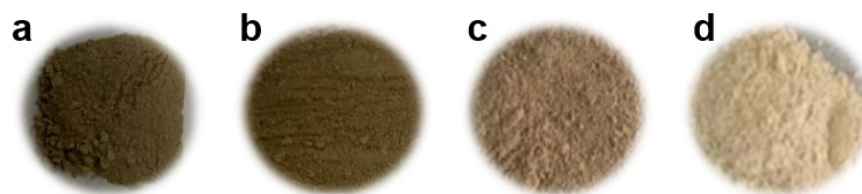


**Figure 4.** Digital photos of (a) KMCZ, (b) KMCZ-300, (c) KMCZ-500 and (d) KMCZ-700.

## 2.2. Structural Characteristics of the Resultant Materials

$\text{N}_2$  adsorption–desorption analysis was performed on a series of samples. The corresponding isotherm curves are presented in Figure 5, and key parameters are summarized in Table 1. The  $\text{N}_2$  adsorption–desorption isotherm of the mesoporous Cr-doped zirconia support (MCZ) exhibits a combination of a Type I isotherm with a distinct H1-type hysteresis loop. The sharp uptake at low relative pressure ( $P/P_0 < 0.1$ ) indicates the presence of some microporosity. The pronounced hysteresis loop in the  $P/P_0$  range of 0.4–0.7 confirms the existence of mesopores. The specific surface area of the MCZ support was  $129 \text{ m}^2 \cdot \text{g}^{-1}$ . The undoped  $\text{ZrO}_2$  support exhibited a comparable BET surface area ( $131 \text{ m}^2 \cdot \text{g}^{-1}$ ) and similar mesoporous characteristics to the MCZ support, confirming that the incorporation of  $\text{Cr}^{3+}$  did not significantly alter the baseline textural properties of the host matrix. After the impregnation of  $\text{KNO}_3$  and subsequent activation at different temperatures, the resulting KMCZ catalysts retained isotherms similar in shape to that of the MCZ support. This observation provides that the proposed low-temperature redox activation strategy successfully preserved the mesoporous framework of support, avoiding the pore collapse typically induced by conventional high-temperature calcination. As listed in Table 1, the specific surface area decreased to  $118 \text{ m}^2 \cdot \text{g}^{-1}$ , which can be attributed to the deposition of  $\text{KNO}_3$  crystals within the pores, increasing pore wall roughness and potentially causing partial pore blocking. When activated at 500 °C, the specific surface area of sample KMCZ-500 reached  $98 \text{ m}^2 \cdot \text{g}^{-1}$ , even slightly exceeding that of the ample KMCZ-300. We attribute this to the complete decomposition of  $\text{KNO}_3$ , which generated highly dispersed  $\text{K}_2\text{O}$  active species, thereby clearing the pores of previously space-occupying bulk  $\text{KNO}_3$  crystals and restoring pore accessibility. However, upon further increasing the activation temperature to 700 °C, the specific surface area of KMCZ-700 decreased to  $23 \text{ m}^2 \cdot \text{g}^{-1}$ . This indicates that the onset of partial sintering and coarsening of the pore walls at this elevated temperature underscores the importance of maintaining the activation temperature below 500 °C for optimal properties.

**Table 1.** Performance parameters of different samples.

| Sample   | $S_{\text{BET}}^a$<br>( $\text{m}^2 \cdot \text{g}^{-1}$ ) | $V_p^a$<br>( $\text{cm}^3 \cdot \text{g}^{-1}$ ) | Amount of Basic Sites ( $\text{mmol} \cdot \text{g}^{-1}$ ) |          |
|----------|------------------------------------------------------------|--------------------------------------------------|-------------------------------------------------------------|----------|
|          |                                                            |                                                  | Theoretical <sup>b</sup>                                    | Measured |
| MCZ      | 129                                                        | 0.17                                             | 0                                                           | 0.13     |
| KMCZ     | 118                                                        | 0.16                                             | 0                                                           | 0.11     |
| KMCZ-300 | 96                                                         | 0.12                                             | 1.98                                                        | 0.82     |
| KMCZ-500 | 98                                                         | 0.12                                             | 1.98                                                        | 1.95     |
| KMCZ-700 | 23                                                         | 0.02                                             | 1.98                                                        | 1.92     |

<sup>a</sup>  $S_{\text{BET}}$ : BET surface area,  $V_p$ : total pore volume. <sup>b</sup> Theoretical values were calculated based on the amount of  $\text{KNO}_3$  loaded.

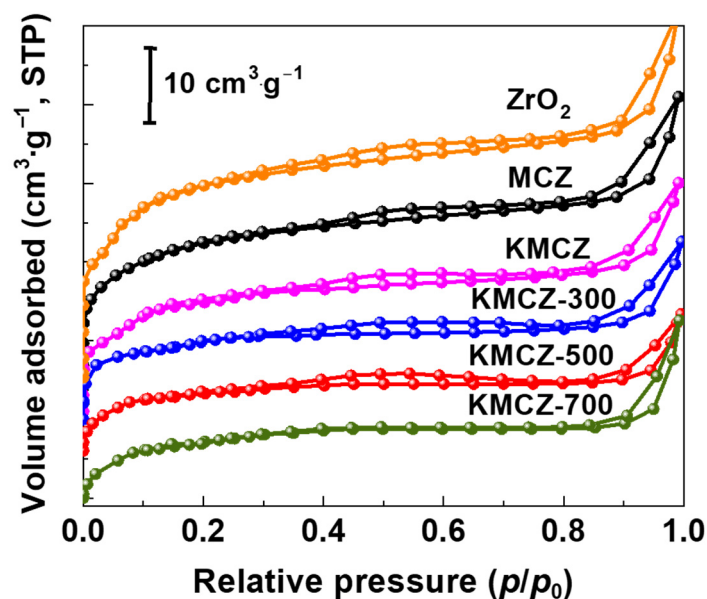


Figure 5. N<sub>2</sub> adsorption–desorption isotherms of the samples.

The KMCZ-500 catalyst was further visualized by SEM and corresponding EDX mapping. The SEM images (Figure 6a) reveal that the material exhibits a loose and porous morphology. More critically, the EDX elemental mapping results (Figure 6b–f) clearly demonstrate a highly homogeneous distribution of zirconium (Zr), oxygen (O), potassium (K), and chromium (Cr) throughout the observed area, with no noticeable regions of elemental aggregation or segregation. This provides that the Cr species were successfully and uniformly incorporated into the zirconia matrix, rather than existing as separate chromium oxide phases, which is fully consistent with the absence of impurity peaks in the XRD patterns. The homogeneous distribution of K also confirms the excellent dispersion of the active K<sub>2</sub>O component on the support surface, which is crucial for exposing abundant basic sites. It is noteworthy that long-range, highly ordered two-dimensional hexagonal mesopores were not observed via TEM. We attribute this to two probable factors. First, the doping of Cr<sup>3+</sup> ions may have subtly altered the co-assembly driving force between the zirconia precursor and the template, affecting the final regularity of the mesostructure. Second, the relatively thin walls of the mesoporous zirconia might be susceptible to partial structural damage during the ultrasonic dispersion required for TEM sample preparation and under irradiation by the high-energy electron beam, making it difficult to resolve perfect periodic features. Nevertheless, by combining the long-range crystalline phase confirmed by XRD, the mesoporous texture determined by N<sub>2</sub> physisorption, and the atomic-level homogeneity of elements demonstrated by EDX mapping, we can confidently conclude that the synthesized KMCZ catalysts successfully achieved uniform loading of active components and effective preservation of the mesoporous framework, providing a solid structural foundation for their exceptional catalytic performance.

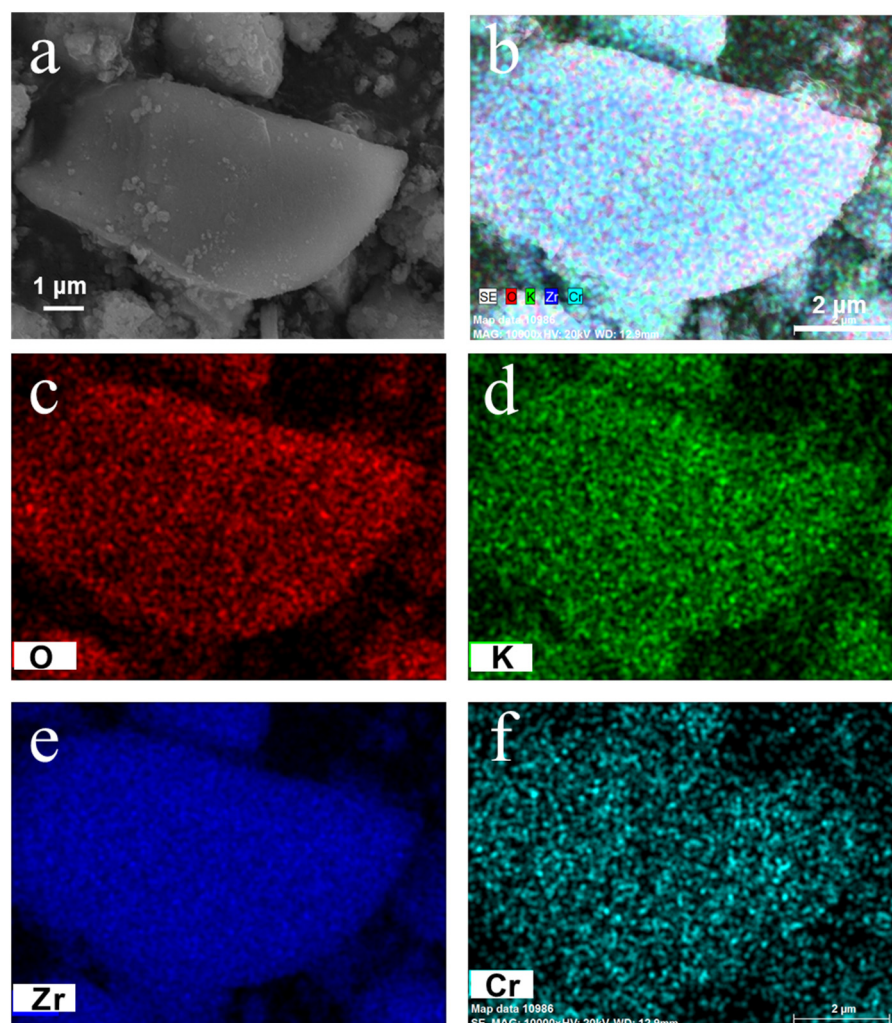


**Figure 6.** (a) SEM and (b–f) EDX-mapping of the sample KMCZ-500.

### 2.3. Basic Properties and Catalytic Performance

The concentration and strength of basic sites are fundamental properties determining the efficacy of a solid base catalyst. The total number of basic sites was first quantified via acid-base titration (Table 1). The bare MCZ support exhibited negligible basicity, confirming its chemical inertness as a host matrix. The  $\text{KNO}_3$ -loaded but unactivated precursor (KMCZ) showed a similarly minimal value of  $0.11 \text{ mmol}\cdot\text{g}^{-1}$ , demonstrating that simple impregnation does not generate active sites. Activation at  $300^\circ\text{C}$  (KMCZ-300) increased the basicity to  $0.82 \text{ mmol}\cdot\text{g}^{-1}$ , corresponding to the partial decomposition of  $\text{KNO}_3$  observed by TG-MS and XRD. A decisive increase occurred at  $500^\circ\text{C}$ : KMCZ-500 reached a basicity of  $1.95 \text{ mmol}\cdot\text{g}^{-1}$ , which is in excellent agreement with the theoretical value of  $1.98 \text{ mmol}\cdot\text{g}^{-1}$  calculated for the complete conversion of all loaded  $\text{KNO}_3$  to  $\text{K}_2\text{O}$ . The quantitative agreement between the measured basicity and the theoretical value for  $\text{K}_2\text{O}$  formation, combined with the high-temperature  $\text{CO}_2$  desorption profile and the absence of crystalline carbonate/hydroxide phases in XRD strongly supports that the generated active phase is highly dispersed  $\text{K}_2\text{O}$ . This quantitative match provides compelling evidence that the redox interaction on the Cr-doped support facilitates full precursor conversion at this atypically low temperature. Notably, activation at  $700^\circ\text{C}$  (KMCZ-700) yielded a comparable basicity ( $1.92 \text{ mmol}\cdot\text{g}^{-1}$ ), proving that conversion remains complete even under conditions that induce textural sintering. This decoupling of chemical conversion from structural stability underscores that while the redox mechanism ensures low-temperature  $\text{KNO}_3$  decomposition, excessive heat remains detrimental to the porous architecture.

The strength distribution of the basic sites was probed by CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD), as shown in Figure 7a. The profile for the MCZ support showed no significant CO<sub>2</sub> desorption, confirming its lack of basicity. In contrast, the CO<sub>2</sub>-TPD profile of the optimally activated KMCZ-500 catalyst revealed three distinct desorption peaks at 385 °C, 485 °C, and 610 °C. These peaks are designated as  $\alpha$ ,  $\beta$ , and  $\gamma$  sites, corresponding to medium-strength, strong, and very strong basic sites, respectively [25]. The presence of the high-temperature  $\gamma$  peak confirms the generation of very strong basic sites, which are highly desirable for demanding base-catalyzed reactions and underscore the effectiveness of our activation strategy.

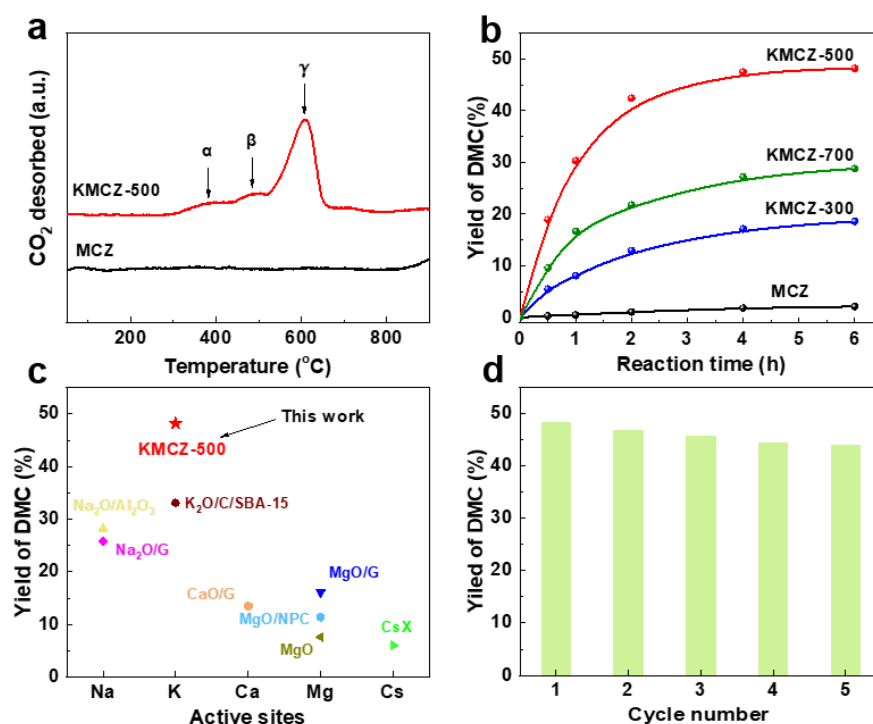


**Figure 7.** (a) CO<sub>2</sub>-TPD profiles of the samples MCZ and KMCZ-500; (b) The yields of DMC under the catalysis of different samples; (c) comparison of catalytic activity with typical reported solid bases; (d) Reusability of the KMCZ-500 as the catalyst for the synthesis of DMC.

The catalytic prowess of the synthesized materials was evaluated in the transesterification of ethylene carbonate with methanol to produce DMC—a pivotal green chemical and fuel additive [50,51]. This reaction serves as a benchmark for solid base catalysts [52,53]. It should be noted that the present study focuses on demonstrating catalytic performance based on DMC yield; a detailed carbon balance analysis quantifying all reaction by-products falls beyond its scope but represents a valuable objective for future mechanistic investigations. The performance trends (Figure 7b) directly mirror the physico-chemical characterization data, revealing clear structure-activity relationships. The inert MCZ support yielded only 2.1% DMC after 6 h. The partially activated KMCZ-300 showed moderate activity (18.6% yield), which correlates linearly with its lower basic site density (0.82 mmol·g<sup>−1</sup>). The optimally activated KMCZ-500 delivered the highest DMC yield of 48.2%, a direct consequence of its combined advantages: the highest density of strong basic sites (1.95 mmol·g<sup>−1</sup>) and a well-preserved, accessible mesoporous network. The case of KMCZ-700 is particularly instructive. Despite possessing a near-identical total basicity (1.92 mmol·g<sup>−1</sup>) to KMCZ-500, its catalytic yield plummeted to 28.8%. This significant drop in activity, despite comparable site numbers, is attributed to the severe textural degradation observed via N<sub>2</sub> physisorption ( $S_{\text{BET}} = 23 \text{ m}^2 \cdot \text{g}^{-1}$ ). The collapsed porosity likely impedes

mass transport, burying a fraction of the active sites and making them inaccessible to reactant molecules. This result highlights a critical principle: for porous solid catalysts, accessibility is as crucial as intrinsic activity.

The superiority of KMCZ-500 was cemented through benchmarking against a range of representative solid base catalysts reported for the same reaction (Figure 7c). Its performance far surpassed that of classic metal oxides like MgO (7.6% yield) and modified systems such as MgO/NPC (11.4%), CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (13.5%), and Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> (28.2%). It also outperformed various advanced carbon-based catalysts and even a strongly basic CsX zeolite (6.0% yield) [21,25,26,54–57]. This comprehensive comparison underscores that our catalyst is not merely an incremental improvement but represents a significant advance in solid base design.

Finally, practical applications demand stability. The reusability of KMCZ-500 was tested over five consecutive reaction cycles (Figure 7d). After a minor initial decrease, the DMC yield stabilized at approximately 42% from the second cycle onward, retaining about 87% of its initial activity. This demonstrates excellent operational stability. The slight deactivation may be attributed to minor leaching of active species or subtle surface reconstruction during the first cycle. The sustained high activity thereafter confirms the robustness of the catalyst's framework and the strong anchoring of the active sites, validating their potential for sustainable catalytic processes.

The formation of Cr (VI) during the activation process necessitates a discussion on environmental and safety aspects for practical application. While this redox state is integral to the proposed low-temperature activation mechanism, its potential leaching and stability under operating conditions are important. It should be noted that the subsequent transesterification reaction is conducted in a strongly reductive medium (methanol) over a strongly basic catalyst. Chromium (VI) is known to be unstable under such reductive conditions and is readily reduced to Cr (III), which has significantly lower solubility and toxicity. Although a dedicated leaching analysis was not performed in this foundational study, the inherent reaction environment suggests a low propensity for Cr (VI) persistence or leakage. The demonstrated good structural and catalytic stability indirectly supports this assessment. For future practical applications, detailed leaching tests (e.g., ICP-MS analysis of post-reaction mixtures) and the design of catalyst encapsulation or stabilization strategies would be essential next steps to ensure full environmental compatibility.

### 3. Experimental Section

#### 3.1. Chemicals

Ultrapure water was used to prepare all solutions. The main reagents, used as supplied, included zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, 98%); Pluronic P123; Cocamidopropyl betaine (CAPB); Chromium (III) nitrate nonahydrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 99%); and potassium nitrate (KNO<sub>3</sub>, 99%).

#### 3.2. Synthesis of Cr-Doped Mesoporous Zirconia

Mesoporous Cr-doped zirconia was synthesized via an evaporation-induced co-assembly method. The zirconium precursor solution (0.25 mol·L<sup>−1</sup>) was prepared by dissolving 2.73 g of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 30 mL of deionized water; separately, 1.0 g of Pluronic P123 and 0.29 g of CAPB (nZr/nCAPB = 1) were dissolved in 10 g of deionized water under stirring to obtain the templating solution. The molar ratio of Zr to P123 was fixed at 100. The templating solution was then added dropwise into the ZrOCl<sub>2</sub> solution at 40 °C under magnetic stirring. After stirring for 30 min to allow preliminary interaction between Zr<sup>4+</sup> ions and the template micelles, an aqueous solution of Cr(NO<sub>3</sub>)<sub>3</sub> (nZr/nCr = 5) was introduced dropwise. The resulting mixture was stirred vigorously for 4 h. Subsequently,

the pH of the mixture was adjusted to 5, followed by continued stirring for another 3 h. The homogeneous gel was transferred into a 50 mL Teflon-lined autoclave and subjected to hydrothermal treatment at 80 °C for 56 h. The resulting solid product was collected by filtration, washed thoroughly with deionized water until the filtration was neutral, and dried at 80 °C for 12 h. Finally, the sample was calcined at 600 °C for 4 h in air to remove the organic templates and crystallize the framework. The material obtained was denoted as MCZ. For comparison, an undoped mesoporous zirconia support (denoted as ZrO<sub>2</sub>) was synthesized using the identical procedure detailed above, but without the addition of the Cr(NO<sub>3</sub>)<sub>3</sub> solution.

### 3.3. Preparation of Solid Base Catalysts

The MCZ-supported catalysts were prepared by wet impregnation. Typically, 0.8 g of the MCZ support was introduced into an aqueous solution containing 0.2 g of dissolved KNO<sub>3</sub> (corresponding to 20 wt.% of the final catalyst in 10 g of deionized water). The mixture was subjected to continuous magnetic stirring for 12 h at ambient temperature. Subsequently, water was removed by evaporation in a water bath maintained at ~75 °C, and the resulting solid was dried overnight at 80 °C to obtain the precursor, denoted as K/MCZ. Activation was carried out by calcining the KMCZ precursor under a N<sub>2</sub> atmosphere at 300, 500, or 700 °C for 4 h, yielding the final catalysts designated as KMCZ-300, KMCZ-500, and KMCZ-700, respectively.

### 3.4. Materials Characterization

Powder X-ray diffraction (XRD) analysis was conducted using a Bruker D8 Advance diffractometer (Bruker, Billerica, MA, USA) equipped with a Cu K $\alpha$  radiation source ( $\lambda = 1.5418 \text{ \AA}$ ). The diffraction patterns were systematically recorded in the  $2\theta$  range of 10–80° under operational parameters of 40 kV and 40 mA. Textural properties were quantitatively evaluated through N<sub>2</sub> physisorption measurements at 77 K using a BSD-660 (BSD Instrument, Beijing, China). Prior to analysis, the samples were degassed under high vacuum condition at 150 °C for 2 h. Fourier transform infrared (FT-IR) spectroscopic measurements were performed on a Nicolet AVATAR-360 spectrometer (ThermoFisher Scientific, Waltham, MA, USA). Catalyst and KBr were prepared by pressing a mixture of 1.5 mg of catalyst and 225 mg of dried KBr into a transparent pellet. Transmission electron microscopy (TEM) was performed on a Thermo Fisher Scientific Talos F200X instrument (Thermo Scientific, Waltham, MA, USA). Scanning electron microscopy (SEM) was conducted using Hitachi Regulus8100 microscope (Hitachi, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha+ spectrometer (Thermo Fisher Scientific, East Grinstead, UK) using a monochromatic Al K $\alpha$  X-ray source. The binding energy scale was referenced to the adventitious carbon C 1s peak at 284.8 eV [58]. Given the strong basicity, surface reaction with atmospheric CO<sub>2</sub>/H<sub>2</sub>O during transfer for ex situ analysis is possible. Thermogravimetric analysis coupled with mass spectrometry (TG-MS) was performed using a NETZSCH STA 449 F5 Jupiter thermal analyzer (NETZSCH-Gerätebau GmbH, Selb, Germany) connected to a QMS 403 D Aëolos quadrupole mass spectrometer (NETZSCH-Gerätebau GmbH). CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) was performed using a BELCAT-A analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA) coupled with a Hiden HAL 201 mass spectrometer (Hiden Analytical Ltd., Warrington, UK) for gas analysis. Typically, 50 mg of the catalyst was loaded into a quartz tube and pretreated under a 20 mL·min<sup>−1</sup> argon flow by heating to 500 °C (10 °C·min<sup>−1</sup>) and holding for 3 h, then cooled to 50 °C. The sample was subsequently exposed to a 10 vol% CO<sub>2</sub>/Ar mixture (total flow: 20 mL·min<sup>−1</sup>) at 50 °C for 1 h for adsorption. After adsorption, physically

bound CO<sub>2</sub> was removed by purging with argon at 50 °C for 1 h. The TPD profile was recorded by heating the sample from 50 °C to 900 °C at a ramp rate of 10 °C·min<sup>−1</sup> under argon flow (20 mL·min<sup>−1</sup>). The MS signal for  $m/z = 44$  (CO<sub>2</sub>) was monitored continuously. The total number of basic sites was measured by acid-based back-titration and is reported in mmol per gram of catalyst. The solid catalyst (50 mg) was first treated with 10 mL of 0.05 M HCl solution and agitated for 24 h to allow complete reaction of the basic sites. The remaining HCl in the filtrate was then titrated against a standardized 0.01 M NaOH solution using phenolphthalein as an indicator. The total basicity was derived from the consumption of HCl.

### 3.5. Catalytic Tests

The transesterification of ethylene carbonate (EC) and methanol to synthesize dimethyl carbonate (DMC) served as a model reaction to assess the catalytic performance. A standard experiment was performed by combining 0.5 mol of methanol, 0.1 mol of EC, and the activated catalyst (0.5 wt.% relative to methanol) in a 100 mL three-neck flask fitted with a condenser and a magnetic stirrer. The reactions were conducted with magnetic stirring at a constant rate of 500 rpm. A preliminary test confirmed that the initial reaction rate became independent of stirring speed above 500 rpm, indicating the absence of external liquid-solid mass transfer limitations under the employed conditions. The mixture was reacted at 65 °C under atmospheric pressure. At predetermined intervals (0.5, 1, 2, 4, and 6 h), approximately 0.2 mL aliquots were extracted from the reaction mixture. These samples were promptly centrifuged for catalyst separation. The resulting clear liquid was analyzed by gas chromatography (Agilent 7890A, Agilent Technologies Inc., Santa Clara, CA, USA) using an HP-5 capillary column and a flame ionization detector (FID). The conversion of EC and the yield of DMC were determined via GC analysis using external calibration. The selectivity to DMC is defined relative to the converted EC. The DMC yield, calculated as the product of EC conversion and DMC selectivity, is reported as the key metric for catalytic performance in the target synthesis. Prior to each catalytic test, the catalyst was activated in situ under a nitrogen flow in a tubular furnace at the target temperature (e.g., 500 °C for KMCZ-500) for 4 h. After cooling under nitrogen to near ambient temperature, the freshly activated catalyst was promptly transferred and charged into the reaction vessel. Although this transfer involved brief exposure to ambient atmosphere, it represents a pragmatic handling condition relevant to potential application.

## 4. Conclusions

This study successfully demonstrates a “carrier reducibility tuning” strategy for the low-temperature construction of efficient solid strong base catalysts. By doping Cr<sup>3+</sup> into a mesoporous zirconia framework, a reducible MCZ carrier was synthesized. A strong redox interaction between this carrier and the supported KNO<sub>3</sub> precursor enabled the complete conversion of KNO<sub>3</sub> at 500 °C. Systematic characterization confirmed that during this low-temperature activation, Cr<sup>3+</sup> was predominantly oxidized to Cr<sup>6+</sup>, while KNO<sub>3</sub> was reductively decomposed, generating highly dispersed strong basic sites. The resulting catalyst exhibited superior activity and stability in the transesterification synthesis of dimethyl carbonate (DMC), outperforming several conventional solid base catalysts. Beyond presenting a high-performance catalyst, this work provides a novel methodology for low-temperature catalyst preparation and offers a fresh perspective on regulating active site formation through the rational design of carrier-precursor interfacial chemistry. Future work should include in situ spectroscopic studies to directly probe the evolution of potassium species during activation, which would provide further mechanistic insight.

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