

Article

Modulating the Hierarchical Pore Structure and Surface Chemistry of Ru/Beta Catalyst by Alkaline Etching to Facilitate the *o*-Dichlorobenzene Oxidation

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Abstract: To resolve issues such as insufficient low-temperature activity and the formation of polychlorinated byproducts during the catalytic combustion of *o*-dichlorobenzene (*o*-DCB), Ru/Beta catalysts were treated with four etching strategies (NaOH, Na₂CO₃, NH₄F, and HNO₃) to modify their pore structure and surface chemistry, thereby elucidating the impact of these etching strategies on catalytic performance. The results indicate that the NaOH etching technique constructed a micro-mesoporous interconnected multi-level pore structure while preserving the integrity of the framework Al, significantly increasing the specific surface area and promoting the high dispersion of Ru species through the grafting effect of the framework Al. NH₃-TPD and H₂-TPR results show that the Ru/Beta-NaOH catalyst possesses both abundant acidic sites and strong redox capabilities. The acidic sites guide Cl species toward the HCl product, effectively suppressing the formation of Cl₂ and polyhalogenated byproducts, while the strong redox ability accelerates the deep oxidation of *o*-DCB. Molecular dynamic simulations further indicate that the hierarchical pore structure effectively alleviates the diffusion limitation of polyhalogenated byproducts, enabling a facilitated reaction. Compared to the unetched Ru/Beta catalyst, the Ru/Beta-NaOH catalyst exhibits a 50 °C lower activation temperature, with a significant reduction in polychlorinated byproducts and improved stability. This catalyst achieves synergistic optimization of active sites and pore engineering, providing a theoretical basis for the development of catalysts for the efficient degradation of macromolecular chlorinated aromatics.

Keywords: *o*-dichlorobenzene oxidation; etching; Ru species; zeolites; hierarchical pores

1. Introduction

Chlorinated aromatic hydrocarbons (CAHs) are a typical category of chlorinated organic pollutants and have been designated as priority pollutants by the U.S. Environmental Protection Agency (EPA) [1]. These compounds generally exhibit bioaccumulation, environmental persistence and significant toxicity, representing typical recalcitrant substances among atmospheric pollutants [2,3]. Catalytic combustion has become one of the most widely used purification technologies due to its high degradation efficiency and minimal secondary pollution [4,5]. The core of this technology lies in the development of highly efficient and stable catalysts [6]. However, a key challenge limiting the practical application of catalytic oxidation is that catalysts are prone to deactivation due to



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chlorine poisoning in a chlorinated atmosphere, and the formation of polychlorinated byproducts during the reaction, which further reduces degradation efficiency. As the most representative class of CAHs, the efficient catalytic removal of polychlorinated benzenes (PhCl_x) has become a major focus of current research in the field of environmental catalysis.

Over the past few decades, extensive research has been conducted on catalysts for the degradation of PhCl_x . Several studies have focused on the degradation performance of transition-metal-oxide catalysts for PhCl_x . Wang et al. synthesized Mn oxide catalysts with different valence states by controlling the calcination temperature and found that $\gamma\text{-MnO}_2$ performed better than other oxides due to its high specific surface area and surficial oxygen species [7]. However, $\gamma\text{-MnO}_2$ inevitably undergoes chlorination at high temperatures, leading to a decrease in catalytic activity. Cano et al. found that the presence of Co^{2+} significantly enhanced the activity in catalytic combustion of *o*-dichlorobenzene (*o*-DCB) [8]. Further comparisons revealed that the Pd/Co-HMOR catalyst exhibited superior activity and durability compared to the Pd/Co-SZ catalyst under both dry and humid conditions. This excellent performance is primarily attributed to its abundant strong acid sites and higher total acid content. However, this catalyst still suffers from susceptibility to deactivation under high-temperature conditions. Compared to transition-metal catalysts, precious-metal catalysts often exhibit superior low-temperature catalytic activity and higher reaction rates. Babu et al. reported that catalysts using chloride as the Pd precursor exhibited better dechlorination activity and stability than those prepared using $\text{Pd}(\text{NO}_3)_2$ as the precursor, which is related to their improved dispersion and the Pd species (Pd^{n+}) formed on the surface [9]. Chen et al. protected the Pt active sites on a CeO_2 support from exposure to a chlorine-containing environment by introducing a $\text{H}_4[\text{Si}(\text{W}_3\text{O}_{10})_4]$ (HSiW) coating, thereby suppressing the formation of polyhalogenated byproducts [10]. Liu et al. evaluated TiO_2 catalysts loaded with different noble metals (Ru, Pd, Pt, Rh) [11]. The results showed that Ru/ TiO_2 exhibited the highest activity and the lowest levels of polychlorinated byproducts, revealing that the selectivity of noble-metal catalysts in the oxidation of chlorobenzenes is highly dependent on their ability to remove chloride species. The noble metal of Ru inherently possesses the ability to effectively remove Cl species via the Deacon reaction [12]. However, Ru-based systems still tend to generate Cl_2 rather than HCl and are often constrained by cost considerations [13]. In this context, zeolites emerge as ideal supports for noble metals due to their well-ordered pore structures, tunable acidity, and excellent thermal stability. Taralunga et al. investigated the performance of Pt-supported zeolite catalysts in the catalytic degradation of *o*-DCB [14]. Their study revealed that the abundant Brønsted acid sites in the zeolite material combined with its unique microporous confinement effect collectively promoted the efficient catalytic conversion of *o*-DCB. In studies on the degradation of *o*-DCB using ZSM-5 zeolite catalysts, it was demonstrated that hydro-oxidation technology can significantly suppress the total formation of polychlorinated byproducts during the *o*-DCB degradation process. This is attributed to the critical role played by the surface acidity of the catalyst in the hydro-oxidation activity of *o*-DCB [15]. The above studies indicate that the acidic characteristics and pore structure of zeolites play important roles in regulating the removal pathways of chlorine species and promoting the dispersion of Ru species.

However, the intrinsic activity of the catalyst in actual reaction processes depends not only on the dispersion state of the active components and the acidity of the support, but is also closely related to the diffusion efficiency of reactant and product molecules within the pore channels and the accessibility of active sites. The three-dimensional (3D), 12-membered ring (12-MR) straight-channel structure (Beta) provides a favorable reaction pathway for the *o*-DCB, but imposes certain limitations on the mass transfer rate of large-molecule polychlorinated byproducts. At low temperatures, it is unable to achieve a balance between catalytic activity and selectivity [16]. Rationally modulating the pore structure of the zeolite support is an effective strategy for further enhancing the mass transfer efficiency and active site utilization of the catalyst. Yu et al. regulated the distribution and size of mesopores in Beta zeolites through a synergistic mechanism involving cetrimonium bromide (CTAB) and NaOH [17]. The treated zeolites exhibited good retention of acidic sites, and the uniform mesopore distribution resulting from etching significantly improved the dispersion of the active component Pt on the catalyst surface. Jan et al. modified ZSM-5 zeolite with NH_4F to obtain a catalytic material suitable for large molecules [18]. This is attributed to the fact that the fluoride etching technique first removes aluminum species outside the framework, thereby increasing the numbers of both active sites and acidic sites. Zou et al. treated a ZSM-5 foam support with acid etching, increasing the mesoporous volume of the catalyst and enhancing the toluene diffusion rate, thereby enabling Pt/ZF-D to exhibit high activity in the catalytic combustion of toluene [19]. These studies confirm that etching modification techniques can introduce mesoporous structures within microporous materials, facilitating the formation of multi-level pore networks that promote catalytic reactions.

To this end, this study selected Beta zeolite as the research subject and subjected it to post-treatment modification using three different typical etching techniques as follows: alkali etching (NaOH , Na_2CO_3), fluoride etching (NH_4F), and acid etching (HNO_3), thereby constructing Beta-etched supports with distinct multi-level pore

structures and surface chemical properties. A series of Ru/Beta-etched catalysts were then prepared via the impregnation method. Combining various characterization techniques with kinetic simulations, this study systematically investigated the influence of different etching techniques on the pore structure, acidity characteristics, and dispersion state of Ru species in the support. The activity, selectivity, and stability of Ru/Beta catalysts modified by different etching techniques were examined in the catalytic oxidation of *o*-DCB, revealing the intrinsic relationship between etching-induced property changes and catalytic behaviors. By exploring effective approaches to enhance the comprehensive performance of Ru-based zeolite catalysts based on support pore engineering, synergistic design principles centered on hierarchical pore structures, acid retention, and enhanced redox activity were established. This provides a controllable preparation strategy for highly efficient catalysts for the degradation of large-molecule chlorinated aromatics, while also laying the foundation for structural optimization of the catalysts.

2. Experimental

2.1. Etching of Beta

The etching process involves separately mixing 1 g of H-beta and 50 mL of deionized water with 0.2 g of NaOH solution (0.1 mol/L), 4.24 g of Na₂CO₃ solution (0.8 mol/L), 5 g of NH₄F solution (2.7 mol/L), and 3.15 g of HNO₃ solution (1 mol/L). The mixed solution was placed in a water bath at 60 °C and stirred for 30 min. The solution was immediately transferred to an ice-water bath for cooling. After temperature reduction, the solution was vacuum filtered and washed five times with deionized water. The obtained sample was then dried in a vacuum oven at 80 °C.

After drying, the sample was mixed with 100 mL of deionized water and 9.6 g of (NH₄)₂CO₃ solution (1 mol/L). The solution was stirred for 6 h in a water bath at 80 °C to ensure sufficient NH₄⁺ exchange, obtaining the hydrogen-type sample. The cooled mixture was filtered under vacuum and washed. The collected residue was then dried in a vacuum oven at 80 °C for 12 h. Finally, the samples were calcined at 550 °C in a muffle furnace at a heating rate of 5 °C /min for 6 h. The obtained solid samples were denoted as H-Beta-NaOH, H-Beta-Na₂CO₃, H-Beta-NH₄F, and H-Beta-HNO₃, respectively.

2.2. Catalyst Preparation

A series of Ru-based zeolite catalysts with a loading of 0.5 wt.% were prepared using the impregnation method. In a typical process, 1 g of zeolite support (H-Beta-X, where X represents different etching agents) was impregnated with 2.67 mL of RuCl₃ (0.0185 mol/L) solution. After continuous stirring for 6 h, this mixture was placed in a rotary evaporator to remove excess water at 80 °C, subsequently transferred to an 80 °C oven for drying for 12 h. Finally, calcination at 550 °C in a muffle furnace for 6 h yielded the etched Ru/Beta catalysts (Ru/Beta-X).

2.3. Catalyst Characterization

Please refer to Supplementary Text S1 for the characterization methods used in this work.

2.4. Molecular Dynamic Simulation

Materials Studio software (19.1.0-2353) was used to undertake the molecular dynamic (MD) simulations on diverse zeolitic topologies, the details are available in Supplementary Text S2.

2.5. Catalytic Activity

For detailed information on the activity test, refer to Supplementary Text S3.

3. Results and Discussion

3.1. Crystal Structure, Morphology, and Acidity

To verify the crystal structures of the various catalysts, XRD characterization was performed on the samples. Figure 1 shows the XRD patterns of Ru/Beta zeolite catalysts before and after treatment under different etching conditions. It can be observed from the figure that all samples exhibit distinct characteristic diffraction peaks of the Beta zeolite near $2\theta = 7.8^\circ$ and 22.5° , which correspond to the typical BEA-type crystal structure (JCPDS No. 48-0074) [20]. Compared to the unmodified Beta zeolite, the positions of the characteristic peaks in the samples treated with the four different etchants did not show significant displacement, indicating that the etching did not destroy the main framework structure of the Beta zeolite. However, the intensity of the diffraction peaks in all

etchant-treated samples decreased to varying degrees, which is related to the increased number of defect sites or the formation of a few amorphous species during the etching process. At the same time, this difference is also related to the different principles of etching: the two alkaline etchants remove Si atoms from the zeolite, while F etching and acid etching remove Al atoms [21,22].

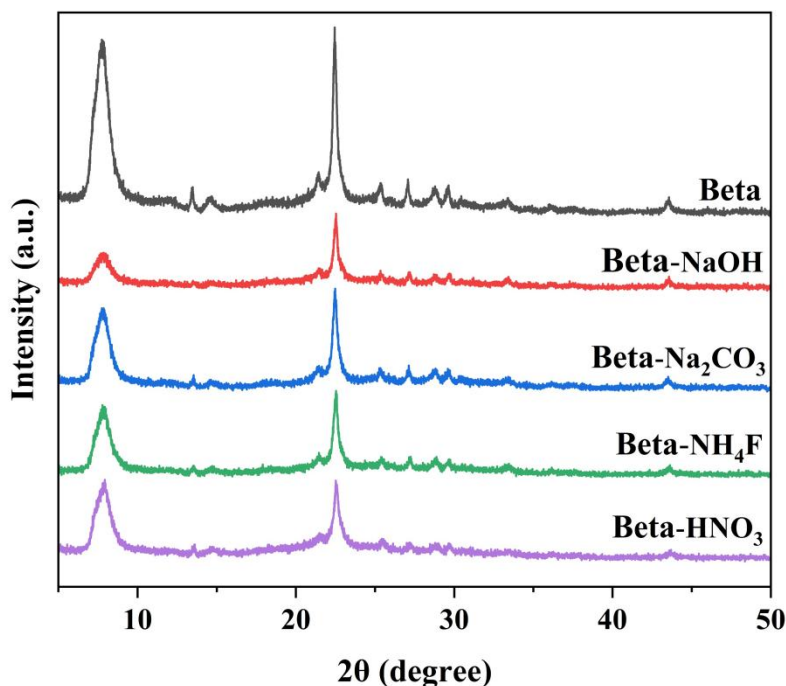


Figure 1. XRD patterns of Ru/Beta catalysts treated with different etching agents.

In Ru/Beta-X (where X is the etchant) catalysts, the characteristic diffraction peaks of RuO₂ (JCPDS No. 43-1027) at 28° and metallic Ru (JCPDS No. 06-0663) at 44.1° were not observed [23,24]. This phenomenon may be due to the relatively low loading of Ru species and the high dispersion of Ru species on the surface or within the pores of the zeolite support via abundant anchoring sites.

As shown in Figure 2, SEM and TEM were performed to investigate the effects of different etching treatments on the catalyst morphology and the distribution of Ru species. Figure 2A,F show the Ru/Beta catalysts before etching. The SEM images reveal that the unmodified catalyst exhibits a nanoparticle morphology characterized by distinct grains, a relatively smooth surface, and uniform grain size. The corresponding TEM images show that RuO₂ particles are uniformly dispersed on the surface of Beta support, with an average particle domain of approximately 5–6 nm and no obvious agglomeration. This indicates that the impregnation method has successfully achieved the initial dispersion of Ru species on the surface of the unmodified Beta support.

The morphology of Beta zeolite undergoes significant changes after NaOH etching. SEM (Figure 2B) shows that the catalyst surface has become somewhat rough. TEM (Figure 2G–I) images clearly reveal uniform and moderate etching marks, which lead to the formation of abundant intergranular or intragranular channels. This highly developed hierarchical pore structure provides an ideal pathway for the rapid diffusion of reactant and product molecules, as well as the effective dispersion of active sites [25]. The particle-size-distribution histogram indicates that RuO₂ particles on the Beta-NaOH surface have a crystal size of approximately 3–4 nm, which is related to the confinement effect of its mesopores on the macromolecular precursor RuCl₃, thereby suppressing the agglomeration of Ru species. In contrast, the etching effect of Na₂CO₃ is relatively mild, the roughness of the Ru/Beta-Na₂CO₃ surface is lower than that of Ru/Beta-NaOH, with only shallow etching pits forming on the surface (Figure 2C). However, the etching traces are not clearly visible in the TEM image (Figure 2J). The particle size of Ru species on its surface remains at 4–5 nm.

The sample etched with NH₄F (Figure 2D) exhibits an extremely irregular topography, with blurred crystal boundaries and enhanced surface roughness. TEM (Figure 2K) clearly reveals etching traces, but their distribution is uneven, indicating that only localized etching occurred. This leads to the agglomeration of Ru particles, with an average grain domain of approximately 7–8 nm. The HNO₃-etched sample exhibits the least morphological change, with a relatively smooth surface (Figure 2E). Corresponding TEM images (Figure 2L) confirm that Ru particles are distributed on the external surface of the zeolite, with an average crystal size of approximately 10–11 nm, indicating poor dispersion.

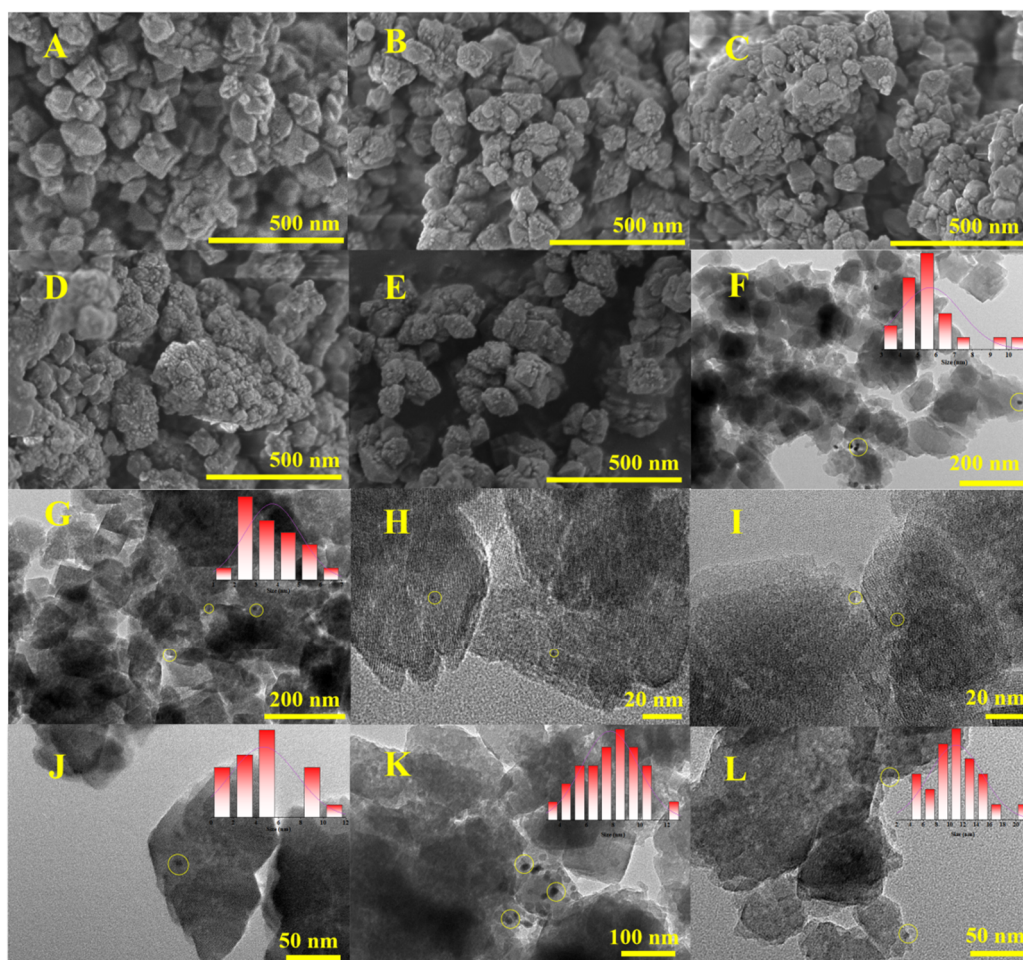


Figure 2. SEM and TEM images of pristine and etched Ru/Beta catalysts: (A,F) Ru/Beta; (B,G,H,I) Ru/Beta-NaOH; (C,J) Ru/Beta-Na₂CO₃; (D,K) Ru/Beta-NH₄F; (E,L) Ru/Beta-HNO₃.

The average particle size of RuO₂ on different catalysts is ordered as follows: Ru/Beta-NaOH < Ru/Beta-Na₂CO₃ < Ru/Beta < Ru/Beta-NH₄F < Ru/Beta-HNO₃. After alkali etching, the Ru particles are smaller and have a more uniform distribution compared to the original catalyst, thereby exposing more active sites and enhancing redox activity [26].

N₂ adsorption-desorption experiment was conducted to demonstrate the sorption curves and pore size distribution of Ru/Beta catalysts with different etching treatments, as shown in Figure 3. The adsorption-desorption curves reveal that all samples exhibit significant N₂ adsorption in the relatively low-pressure region ($P/P_0 < 0.02$), indicating the presence of microporous structures. Among these, the unetched Ru/Beta catalyst exhibits a typical Type I isotherm. Catalysts pretreated with different etchants display characteristic hysteresis loops in the relatively high-pressure region, indicating the successful introduction of mesoporous structures. However, the hysteresis loop of the Ru/Beta-HNO₃ sample is notably smaller, in consistent with its lowest mesoporous volume (Table 1).

Table 1. The surface area and pore volume of Ru/Beta treated with different etching agents.

Sample	S_{BET}^a ($\text{m}^2 \cdot \text{g}^{-1}$)	S_{micro}^b ($\text{m}^2 \cdot \text{g}^{-1}$)	S_{meso}^c ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{total}^d ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{micro}^b ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{meso}^c ($\text{cm}^3 \cdot \text{g}^{-1}$)
Ru/Beta-NaOH	801	552	165	1.17	0.23	0.94
Ru/Beta-Na ₂ CO ₃	717	526	130	0.78	0.21	0.57
Ru/Beta-NH ₄ F	554	439	131	0.72	0.18	0.54
Ru/Beta-HNO ₃	523	423	76	0.50	0.17	0.33
Ru/Beta	690	603	47	0.55	0.24	0.31

^a S_{BET} is calculated by the Brunauer-Emmet-Teller equation. ^b S_{micro} and V_{micro} is calculated by the t -plot method. ^c S_{meso} and V_{meso} is calculated by the Barrett-Joyner-Halenda method. ^d The volume is achieved at $P/P_0 = 0.99$.

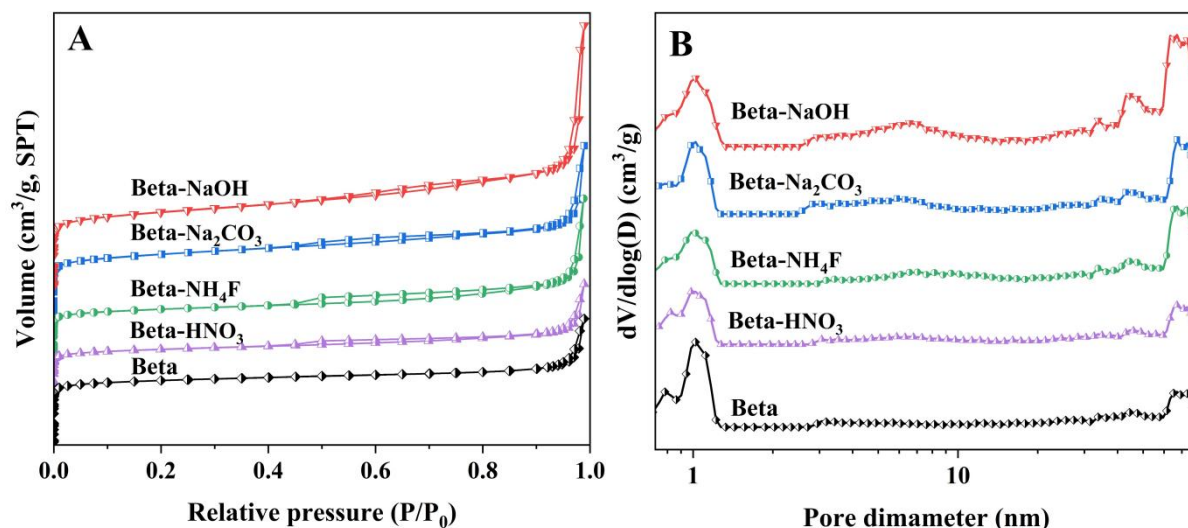


Figure 3. (A) N₂ adsorption-desorption isotherms and (B) pore-size distribution of Ru/Beta catalysts treated with different etching agents.

Combining the pore-size-distribution diagram (Figure 3B) with the data in Table 1 reveals significant differences in the effects of different etching agents on pore structure. The Ru/Beta-NaOH catalyst exhibits a mesoporous distribution within a wide pore-size range of 2–11 nm, indicating that the strong desilication effect of NaOH effectively constructed a developed hierarchical pore network. This facilitates the diffusion of macromolecules, thereby increasing the probability of contact with active components. The mesopores of the Ru/Beta-Na₂CO₃ catalyst are primarily concentrated in a smaller size range (2–8 nm), which is attributed to the mild etching of Na₂CO₃, resulting in a limited creation of mesopores [27]. Although the V_{total} and V_{meso} of the Ru/Beta-NH₄F catalyst are similar to those of the Ru/Beta-Na₂CO₃ catalyst, the connectivity and orderliness of its mesopores could be inferior, as indicated by the uneven etching observed via TEM. The Ru/Beta-HNO₃ catalyst contains very few mesopores, implying its failure to effectively construct a distinct hierarchical pore structure.

The S_{BET} value of the samples is as follows: Ru/Beta-NaOH (801 m²/g) > Ru/Beta-Na₂CO₃ (717 m²/g) > Ru/Beta (690 m²/g) > Ru/Beta-NH₄F (554 m²/g) > Ru/Beta-HNO₃ (523 m²/g). Alkali etching increased the specific surface area, which is attributed to the fact that the contribution of mesopores to the surface area exceeded the loss of micropores. The decrease in specific surface area observed after fluorine etching and acid etching suggests that excessive or inappropriate etching (Al removal) may have caused damage to the skeletal structure or partial pore blockage [28]. Under conditions where the actual Ru loading on each catalyst is similar (Supplementary Table S1), a larger specific surface area facilitates the dispersion of active components and the adsorption of reactants. Therefore, etching techniques that create new mesopores while causing minimal damage to the original microporous framework are more conducive to enhancing the reactivity.

The coordination states of Al species in different modified samples were characterized by ²⁷Al MAS NMR. As shown in Figure 4, two main signal peaks are observed. The strong signal peak at 55 ppm is attributed to tetra-coordinated [Al(IV)] framework Al species (FAL), which can participate in acid regulation and is primarily associated with Brønsted acid sites [29,30]. In contrast, the weak signal peak at 0 ppm is attributed to hexacoordinated [Al(VI)] extra-framework Al species (EFAL) [31]. The relative content of Al species indicates that FAL remains the predominant form before and after etching. Following treatment with different etching agents, the content of EFAL in each catalyst decreased. Among these, the catalyst etched with NaOH retains its framework Al species well due to its strong selective desilication effect. Mild etching with Na₂CO₃ also shows minimal damage to the FAL, with its FAL signal being slightly lower than that of Ru/Beta-NaOH. In contrast, etching with NH₄F and HNO₃ exhibits strong removal capabilities for FAL, resulting in a significant reduction in the FAL signal. Thus, it is evident that alkaline etchants are most conducive to maintaining the integrity of the FAL while constructing mesoporous channels. A high content of FAL promotes the dispersion and stability of Ru nanoparticles through strong metal-support interactions, whereas the presence of excessive EFAL species restricts reactant diffusion and is detrimental to catalytic reactions [32,33]. Therefore, the regulation of the FAL and EFAL content in the zeolite after etching has a critical impact on catalytic performance.

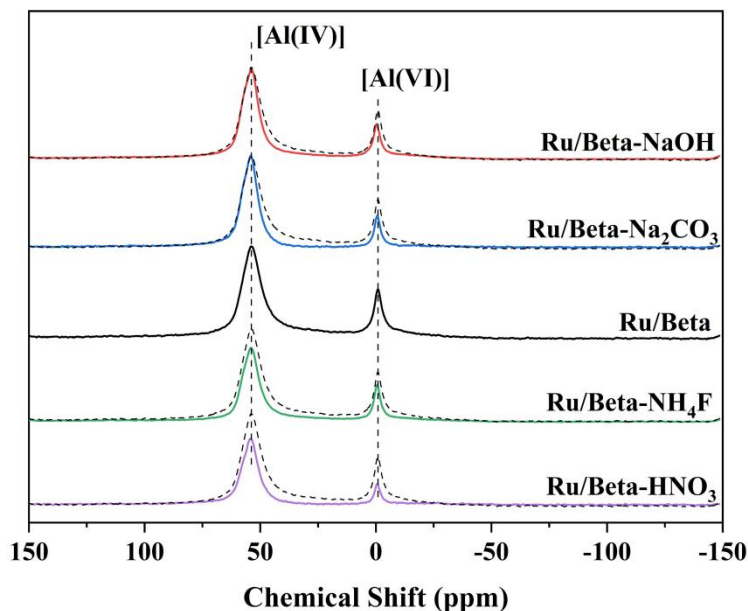


Figure 4. ^{27}Al MAS NMR spectra of Ru/Beta catalysts.

To investigate the effect of different etching agents on the acidity of the catalyst, NH_3 -TPD experiments were conducted on the catalyst before and after modification. The NH_3 desorption curves and quantitative analysis results are shown in Figure 5A. The NH_3 -TPD curves of all catalysts exhibited two distinct characteristic peaks. The NH_3 desorption peaks in the 100–300 °C and 300–600 °C temperature ranges correspond to weak acid sites (primarily related to Lewis acid sites) and strong acid sites (primarily related to Brønsted acid sites), respectively [34]. The weak acid sites are attributed to surface hydroxyl groups (Si-OH and Al-OH), while the strong acid sites are attributed to bridging hydroxyl groups (Al-OH-Si) [35,36]. The total acid content of each catalyst, calculated based on quantitative analysis, is ranked as follows: Ru/Beta-NaOH > Ru/Beta- Na_2CO_3 > Ru/Beta > Ru/Beta- NH_4F > Ru/Beta- HNO_3 . Compared to the Ru/Beta catalyst, the total acid contents of the Ru/Beta-NaOH and Ru/Beta- Na_2CO_3 catalysts increased, while those of the Ru/Beta- NH_4F and Ru/Beta- HNO_3 catalysts decreased sharply, which is consistent with the trend in their Si/Al ratios (Supplementary Table S1).

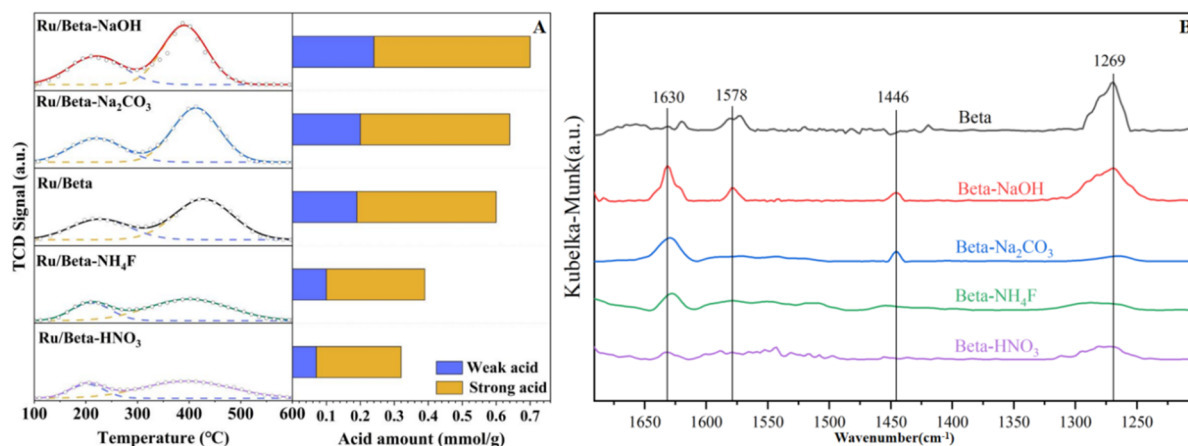


Figure 5. (A) NH_3 -TPD curves and quantitative results of Ru/Beta catalysts treated with different etching agents and (B) In situ DRIFTS spectra of NH_3 adsorption over various catalysts.

The acid properties of various modified Beta zeolites were characterized via infrared spectroscopy (NH_3 -IR) with an exposure to ammonia, and the corresponding results are presented in Figure 5B. A characteristic absorption band centered at 1630 cm^{-1} was observed for all samples, which was assigned to the N-H bending vibration of coordinatively adsorbed NH_3 on Lewis acid sites. The absorption peak at 1446 cm^{-1} corresponded to the N-H bending vibration of protonated NH_4^+ species anchored on Brønsted acid sites, while the band at 1578 cm^{-1} was a secondary peak related to Lewis acid sites, which could indirectly reflect the variation in the signal intensity of Lewis acid. The pristine Beta zeolite possessed a low content of acid sites and only exhibited extremely weak Lewis acid signals. After NaOH modification, the absorption intensity at 1630 cm^{-1} increased remarkably,

revealing that the desilication induced by strong alkali treatment generated abundant framework defects and thus greatly increased the number of Lewis acid sites. Meanwhile, distinct Brønsted acid signals were detected at 1446 cm^{-1} , which originated from residual proton sites that remained unetched or newly exposed during the etching process. The Lewis acid intensity of Na_2CO_3 -modified samples was between those of pristine Beta and NaOH -modified counterparts, demonstrating that weak alkali treatment exerted a milder effect on generating Lewis acid sites. In comparison, NH_4F modification only introduced a small amount of Lewis acid sites, and no obvious Brønsted acid signals were detected. For HNO_3 -modified samples, no prominent characteristic acid-related peaks were observed at 1630 cm^{-1} and 1446 cm^{-1} , indicating that nitric acid treatment almost eliminated all detectable acid sites. In addition, the parent Beta zeolite displayed the strongest framework characteristic peak at 1269 cm^{-1} , whereas the intensity of this peak decreased to varying degrees for all modified samples. Among them, the attenuation of peak intensity was most significant for NaOH and HNO_3 -modified samples, confirming that the modification treatments caused certain damage to the framework structure of Beta zeolite. The NH_3 -IR results were highly consistent with those obtained from NH_3 -TPD measurements. It was further verified that alkali-induced desilication could open the sealed pore channels of zeolites and expose the shielded acid sites, thereby providing sufficient active acid sites for the improvement of HCl selectivity.

The higher acid content of the Ru/Beta- NaOH catalyst is attributed to significant loss of silicon atoms during the NaOH etching process [17]. The intrinsic mechanism for the superior acid content of the Ru/Beta- NaOH sample can be further clarified based on the Al NMR results. As illustrated in Figure 4, the samples treated with acidic etching (NH_4F and HNO_3) exhibit much lower concentrations of extra-framework Al (EFAL) than those modified by alkaline etching (NaOH and Na_2CO_3). Acidic treatment barely removes the silicon framework but enables deep penetration of acidic species into the zeolite matrix, thereby inducing severe etching and loss of framework Al species. The substantial depletion of Al significantly reduces the number of bridging hydroxyl groups, which serve as strong acid sites, thereby accounting for the low acidity of the NH_4F - and HNO_3 -treated samples. In contrast, alkaline etching preferentially removes the silicon framework while causing negligible damage to Al species, which is well supported by the variation in bulk Si/Al ratio. The Si/Al ratio decreases from 12.5 for parent Beta to 9.2 for the NaOH -etched sample. The selective removal of silicon skeleton effectively exposes abundant previously shielded strong acid sites inside the zeolite, which endows the Ru/Beta- NaOH sample with the highest acid content among all catalysts.

Furthermore, the Brønsted acid content is ranked as follows: Ru/Beta- NaOH > Ru/Beta- Na_2CO_3 > Ru/Beta > Ru/Beta- NH_4F > Ru/Beta- HNO_3 . Brønsted acid sites promote both the adsorption of *o*-DCB and the cleavage of the C-Cl bond [37]. The framework Al content plays a regulatory role in ensuring the Brønsted acid content, as significant loss of framework Al directly impairs the formation of Brønsted acid sites resulting in declined content. The alkaline etching treatment caused a slight decrease in the framework Al content, but its effective etching action successfully opened the pores, exposing previously masked acidic sites. Consequently, the number of Brønsted acid sites actually increased. In addition, the order of Lewis acid content is identical to that of Brønsted acid content. Abundant Lewis acid sites can also facilitate dechlorination and C-C bond cleavage, further enhancing the low-temperature activity of the catalyst [38]. Therefore, the synergistic effect of Brønsted acid and Lewis acid sites not only promotes Cl desorption and prevents catalyst poisoning but also increases the conversion rates of reactants and intermediates.

3.2. Characterization of Ruthenium and Oxygen Species

The redox property of the catalyst is one of the key factors determining the efficiency of *o*-DCB catalytic degradation [39,40]. To investigate the effect of different etching techniques on the redox behaviors of catalysts, H_2 -TPR experiments were conducted on all samples, as shown in Figure 6. The H_2 consumption of each sample is presented in Supplementary Table S2. H_2 consumption reflects the relative abundance of reducible species. The H_2 consumption values for all samples were similar, which is attributed to the use of the same rotary evaporation preparation process. This process ensures that Ru species are theoretically fully loaded onto the support. Consequently, the actual Ru loading on each sample is comparable as confirmed by ICP analyses (Supplementary Table S1). The onset temperature of the H_2 reduction peak reflects the ease with which the active species is reduced, with a lower onset temperature indicating that the active species is more easily reduced and has a smaller particle size [41]. This represents its stronger redox capability. From the H_2 -TPR data, it can be seen that the onset temperatures of the peaks corresponding to the reduction of RuO_2 to metallic Ru for different catalysts are as follows: Ru/Beta- NaOH ($147\text{ }^\circ\text{C}$) < Ru/Beta- Na_2CO_3 ($156\text{ }^\circ\text{C}$) < Ru/Beta ($159\text{ }^\circ\text{C}$) < Ru/Beta- NH_4F ($163\text{ }^\circ\text{C}$) < Ru/Beta- HNO_3 ($182\text{ }^\circ\text{C}$). The catalysts treated with alkali etching exhibit a lower reduction temperature with respect to the Ru/Beta catalyst.

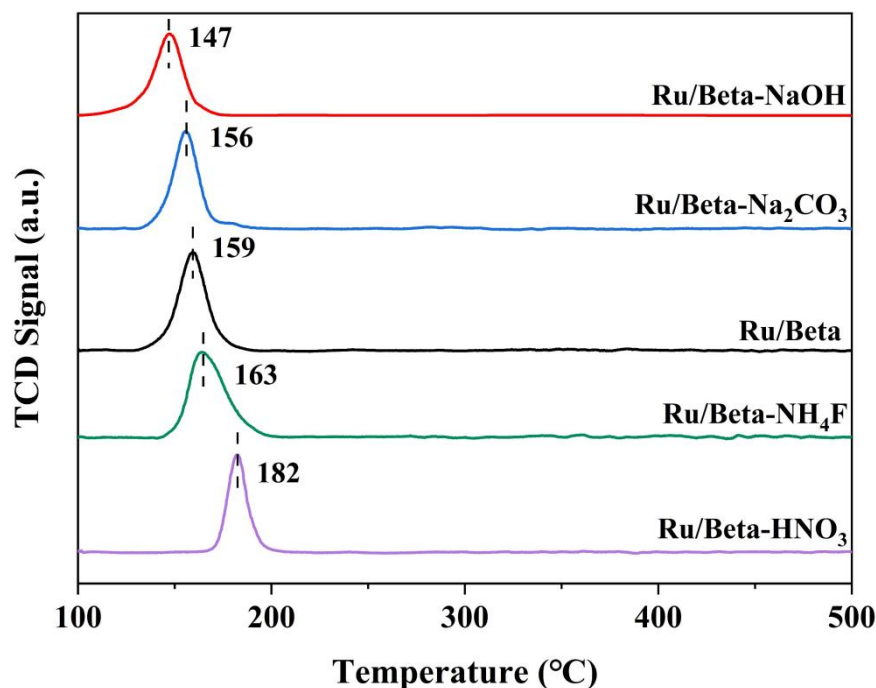


Figure 6. H₂-TPR profiles of Ru species of the Ru/Beta catalysts treated with different etching agents.

The reduction behavior of Ru species on the zeolite is significantly influenced by their dispersion state and interactions with the carrier [42]. At the same time, the introduction of mesoporous structures can confine Ru species during the preparation process, promoting their dispersion. The lowest reduction temperature of Ru/Beta-NaOH is attributed to its smallest particle size (3–4 nm) and well-developed mesoporous network, as well as the high retention of framework Al species, which further promotes the dispersion of Ru species through metal-support interactions. Na₂CO₃ exhibits weaker etching properties than NaOH, resulting in diminished redox capacity. As for the Ru/Beta-NH₄F and Ru/Beta-HNO₃ catalysts, due to the presence of fewer framework Al species or poor pore connectivity caused by blockage, highly dispersed Ru species cannot be obtained. This finding is consistent with the TEM results, leading to redox capacities that are weaker than that of the original catalyst.

As shown in Figure 7A, the XPS spectra of all samples before and after etching with different etchants are presented, specifically focusing on the analysis of the O 1s orbitals. According to the literature, the binding energy peak at 530.0 ± 0.2 eV is attributed to surface-adsorbed oxygen species (denoted as O_α), including oxygen adsorbed at defect sites and weakly bound oxygen species [43]. These oxygen species typically possess high mobility and reactivity capabilities [44]. Their mobility plays a key role in oxidation reactions, and the adsorbed gaseous oxygen can also replenish the oxygen consumed during the catalytic process, thereby enhancing catalytic activity [45,46]. The binding energy peak at 531.2 ± 0.2 eV corresponds to bridging oxygen within the zeolite framework (Si-O-Si and Si-O-Al) or surface hydroxyl groups (denoted as O_β), reflecting the intrinsic framework structure of the support. Additionally, the relative abundances of various elements on the catalyst surface are shown in Supplementary Table S3. Among them, Ru/Beta-NaOH exhibits the highest O_α/O_β ratio, which is attributed to the creation of abundant defect sites and pore structures on the catalyst surface due to its strong etching effect. The etching effect of Na₂CO₃ is weaker than that of NaOH, resulting in slightly lower surface-adsorbed oxygen species. The O_α content is also closely related to the S_{BET} of the catalyst. Following fluorine etching and acid etching, the surface structure of the catalyst was disrupted and its S_{BET} decreased, leading to a lower proportion of O_α compared to the Ru/Beta catalyst. A high proportion of O_α indicates that the catalyst surface possesses more active oxygen species capable of participating in oxidation reactions, which is more conducive to the deep oxidation of *o*-DCB.

Figure 7B shows the O₂-TPD test results for different catalysts. The O₂-TPD profiles of Ru/Beta catalysts treated with different etching agents were investigated to identify the nature and reactivity of surface oxygen species. Two distinct desorption regions were observed: the low-temperature α-O region (167–220 °C) assigned to weakly adsorbed oxygen species and the medium-temperature β-O region (313–341 °C) attributed to chemically adsorbed oxygen and surface lattice oxygen associated with highly dispersed RuO_x sites. Acid-treated samples exhibited higher desorption temperatures for both α-O and β-O peaks, indicating stronger oxygen binding to the catalyst surface. In contrast, alkali-treated catalysts showed significantly lower desorption temperatures, suggesting weakened metal-oxygen interactions and enhanced oxygen mobility. XPS results (Table S3) directly correlate with the relative intensity of the low-temperature α-O peak in the O₂-TPD profiles, confirming that alkali

etching increases the proportion of weakly adsorbed, reactive oxygen species. Such species are critical for oxidation reactions, as they can be readily activated and participate in catalytic cycles at moderate temperatures. Conversely, acid treatment reduces the content of weakly adsorbed oxygen and strengthens metal-oxygen interactions, which may suppress catalytic performance by limiting oxygen availability.

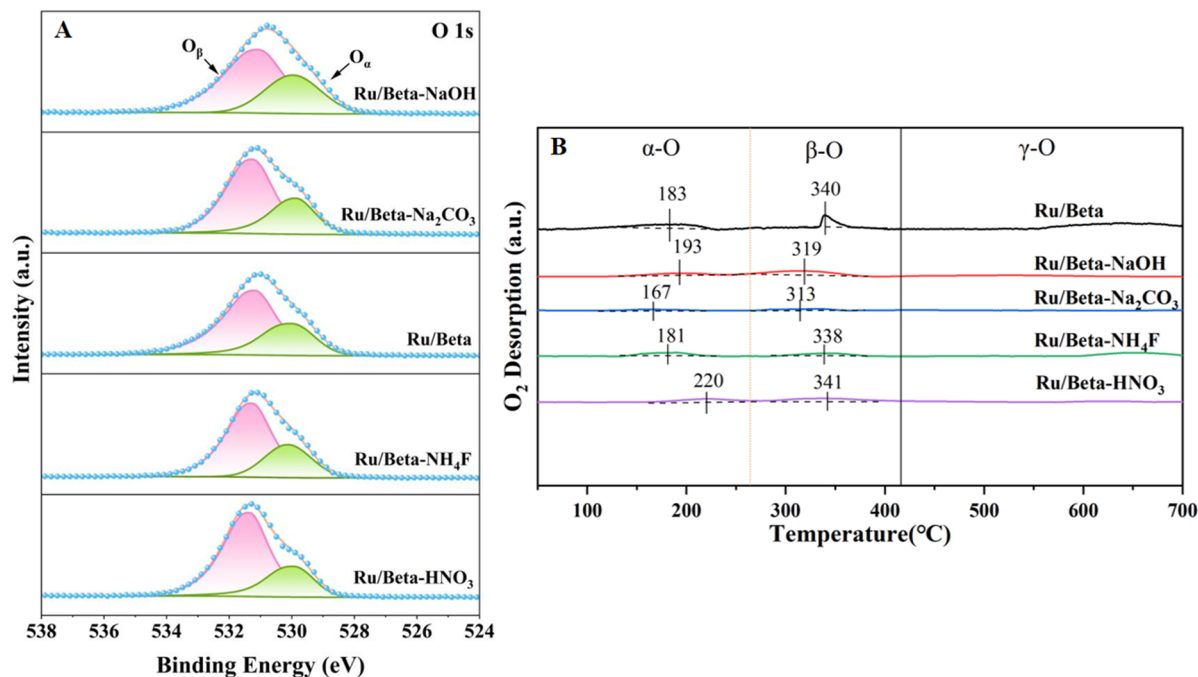


Figure 7. (A) O 1s XPS spectra and (B) O₂-TPD profiles of Ru/Beta catalysts treated with different etching agents.

3.3. Catalytic Activity, By-Product Distribution, and Long-Term Test of Catalysts

To systematically evaluate the effects of different etching treatments on the catalytic performance of Ru/Beta catalysts in the oxidation of *o*-DCB, the catalytic activity of each catalyst toward *o*-DCB and the yields of the target products CO₂ and HCl were investigated, as shown in Figure 8. Figure 8A presents the curve of *o*-DCB conversion as a function of reaction temperature. Overall, the *o*-DCB conversion of all catalysts gradually increased with rising temperature. Notably, the activation temperatures of the etched catalysts were all shifted to 250 °C, indicating that the mesoporous structure introduced by etching effectively promoted contact and reaction between *o*-DCB molecules and active sites within the pore channels, thereby enhancing low-temperature activity.

It is worth noting that different etching strategies result in markedly different trends in activity. To compare catalytic activity more accurately, the activity ranking of the catalysts at 350 °C is as follows: Ru/Beta-NaOH > Ru/Beta-Na₂CO₃ > Ru/Beta > Ru/Beta-NH₄F > Ru/Beta-HNO₃. A multi-criteria evaluation of the catalytic activity of each catalyst clearly reveals the fundamental differences between the two etching pathways: the alkaline etching technique for desilication introduces mesopores while preserving the Al framework to the greatest extent, thereby enhancing activity. Conversely, the etching techniques for Al removal (NH₄F, HNO₃) disrupt the integrity of the Al framework, leading to a decrease in activity. This further supports the conclusion that Al species influence catalytic performance by regulating metal-support interactions. Al species play a crucial role in the *o*-DCB catalytic elimination [16]. Among these, the Ru/Beta-NaOH catalyst exhibited the best low-temperature activity and the highest conversion, achieving a conversion of 10% at an activation temperature of 250 °C, which was lower than those of other catalysts. At 350 °C, the *o*-DCB conversion reached over 95%, about 10% higher than that of the unetched Ru/Beta catalyst. This superior activity is attributed to the combined effects of its remarkable redox capability and multilevel pore structure.

Figure 8B,C show the CO₂ and HCl yields for each catalyst, reflecting their deep oxidation capabilities and their ability to regulate the removal pathways of chlorine species, respectively. The order of target product yields for each catalyst is generally consistent with the order of *o*-DCB conversion rates. Furthermore, it is evident that at lower temperatures (250–300 °C), the etched catalysts exhibit notably superior target product yields compared to the pristine catalysts. This can be attributed to the etching treatment creating defect sites on the zeolite surface, which effectively enrich surface-adsorbed oxygen (O_α), thereby promoting the generation of reactive oxygen species and enhancing the efficiency of the deep oxidation reaction [47]. However, when the reaction temperature rises above 350 °C, the target product yields of the Ru/Beta-NH₄F and Ru/Beta-HNO₃ catalysts are lower than that

of the Ru/Beta catalyst, achieving CO₂ and HCl yields above 95% only at 450 °C. This phenomenon occurs because at lower temperatures, the positive effect of mesopores allows reactant molecules and various large chlorinated intermediates to diffuse and react smoothly within the pore channels, so the chlorination effect is not yet pronounced. However, as the reaction temperature continues to rise, Cl species accumulate on the catalyst surface. Combined with the relatively weak acidity of these two catalysts, this makes it difficult to remove the Cl species in the form of HCl, thereby inhibiting the increase in the yield of the target products.

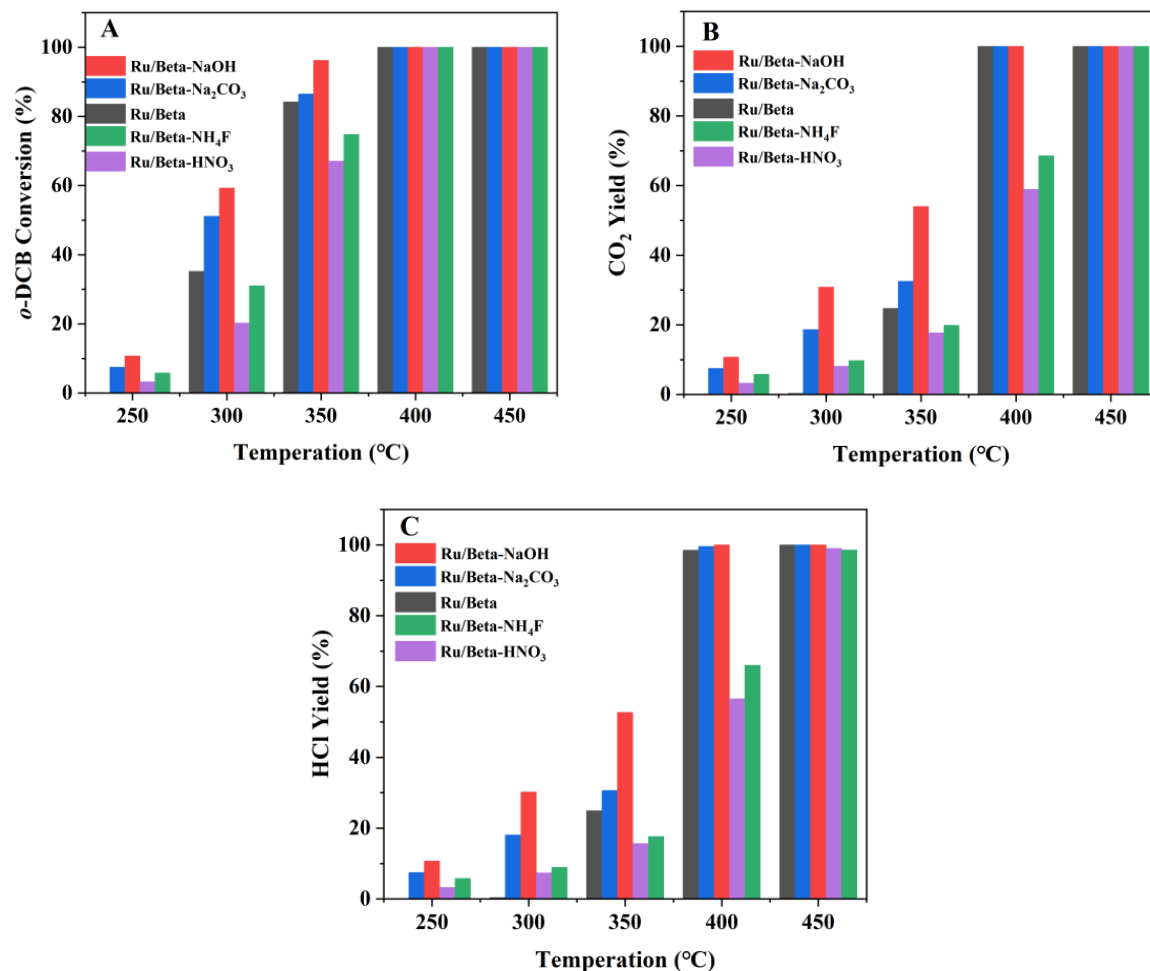


Figure 8. Thermal start-up bar charts of catalytic performance over Ru/Beta catalysts treated by different etching agents: (A) *o*-dichlorobenzene (*o*-DCB) conversion, (B) CO₂ yield, (C) HCl yield. Reaction conditions: 1000 ppm *o*-DCB, 10 vol.% O₂, balanced with N₂, GHSV = ~40,000 h⁻¹.

In the *o*-DCB catalytic oxidation process, in addition to conversion of reactant and yield of the target product, the examination of various byproducts (particularly chlorinated byproducts) cannot be overlooked. These byproducts not only reflect the selectivity of the reaction pathway but also reveal the ability of the catalyst to remove chlorine species and its resistance to chlorine poisoning. If chlorinated byproducts are not completely dechlorinated and converted, they not only pose a risk of secondary pollution but also cause catalyst deactivation due to their strong adsorption and accumulation on the catalyst surface [48]. Therefore, a comprehensive analysis of the types and distribution patterns of byproducts is crucial for the optimized design of catalysts. Figure 9 illustrates the effect of different etching treatments on the yields of byproducts.

As a product of incomplete oxidation, the amount of CO generated is related to the oxidative ability of the catalyst. As shown in Figure 9A, the CO yield for all catalysts initially increased and then decreased to 0% at 400 °C, while the overall CO yield for all catalysts remained below 2% throughout the process. This indicates that all catalysts possess ideal oxidation capabilities for the small molecule intermediates formed after benzene ring opening. The formation of Cl₂ reflects the removal of Cl species via undesired pathways. Furthermore, Cl₂ reacts with *o*-DCB in a chlorination reaction to form more toxic polychlorinated byproducts such as trichlorobenzene, tetrachlorobenzene, and pentachlorobenzene, as shown in Figure 9D–F. Among all catalysts, the Ru/Beta-NH₄F and Ru/Beta-HNO₃ catalysts showed consistently higher Cl₂ yields than the Ru/Beta catalyst throughout the

catalytic process due to their scarcity of acidic sites. In contrast, the alkali-etched catalysts featuring abundant acidic sites achieved a zero Cl_2 yield before the pristine catalyst. This fully demonstrates that acidic sites function as crucial drivers in promoting the conversion of Cl species to the desired HCl [49].

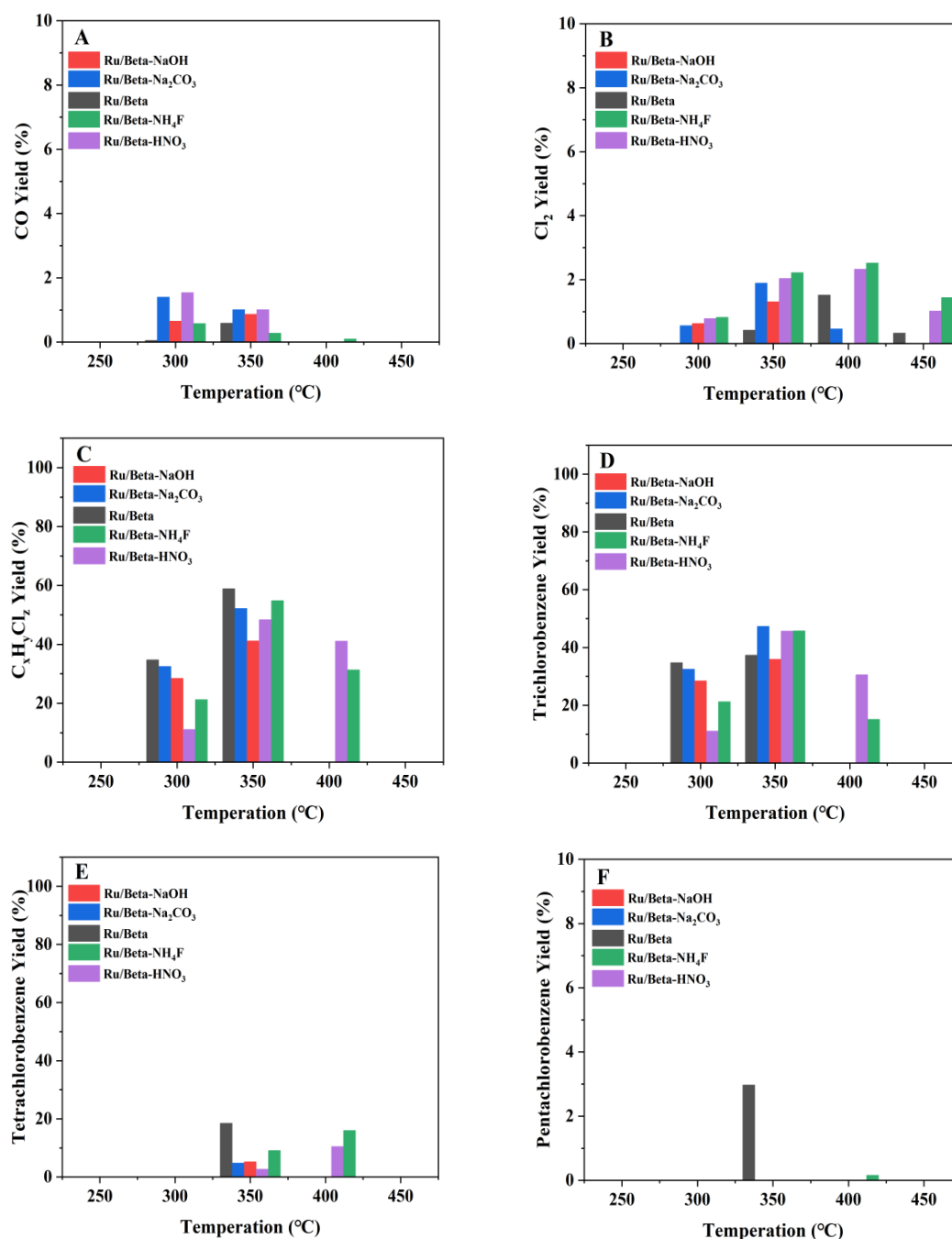


Figure 9. The yields of by-products: (A) CO, (B) Cl_2 , (C) $\text{C}_x\text{H}_y\text{Cl}_z$ (including trichlorobenzene, tetrachlorobenzene, and pentachlorobenzene), (D) trichlorobenzene, (E) tetrachlorobenzene, and (F) pentachlorobenzene, over Ru/Beta catalysts treated with different etching agents. Conditions: 1000 ppm *o*-DCB, 10 vol.% O_2 , balanced by N_2 , GHSV = $\sim 40,000 \text{ h}^{-1}$.

The formation of polychlorinated benzenes during the catalytic process reflects the capability of the catalyst to suppress secondary chlorination reactions and to facilitate ring-opening oxidation [50]. As shown in Figure 9C, the polychlorobenzene yield exhibits a volcano-shaped curve with respect to temperature. The acidity of the catalyst effectively reduces Cl_2 formation, thereby suppressing the chlorination reaction. However, at the peak temperature of 350 °C, the polychlorobenzene yields of all etched catalysts are lower than that of the pristine Ru/Beta catalyst. This is because the mesoporous channels created by etching effectively alleviate the diffusion constraints of bulky molecular byproducts within the zeolite, allowing active sites inside the zeolite channels to be

fully utilized. This facilitates the ring-opening reaction, thereby reducing the formation of chlorinated byproducts. This phenomenon indicates that the pore structure plays a more dominant role in the catalytic reaction with respect to acidity. This finding is consistent with the view of the prerequisite role of pore structure proposed in previous studies [16]. The important role of acidity is evident in the high-temperature reaction occurring above 350 °C. Alkali-etched catalysts and the original catalyst with good acidity exhibit a sharp decrease in the yield of polychlorinated byproducts in the 350–400 °C temperature range until they are completely degraded. In contrast, the byproduct yields for fluorine etched and acid etched catalysts remain as high as 30% at 400 °C. This comparison clearly demonstrates that sufficient acidic sites also play a key role in achieving the deep dechlorination and degradation of polychlorinated byproducts.

As shown in Figure 10, to evaluate the stability of the Ru/Beta-NaOH and Ru/Beta catalysts under prolonged reaction conditions, continuous catalytic oxidation of *o*-DCB was conducted for 30 h at 400 °C. Throughout the entire reaction period, the Ru/Beta-NaOH catalyst consistently maintained a 100% conversion for *o*-DCB (Figure 10A). As shown in Figure 10B, the Ru/Beta-NaOH catalyst maintained a stable 100% yield for the target products CO₂ and HCl for up to 14 h. Starting from the 15th hour, the yields began to decline slowly, however, remained at high levels of approximately 85% and 95% until the 30th hour. Compared with the unetched Ru/Beta catalyst (Figure 10C,D), the decline in Ru/Beta-NaOH is significantly reduced, demonstrating excellent long-term stability. Furthermore, the yield of polychlorinated byproducts remained at an extremely low level throughout the entire test cycle. By the 30th hour, the total yield of polychlorinated byproducts was only about 5%, lower than that of the Ru/Beta catalyst during the same period. This indicates that Ru/Beta-NaOH not only maintains high activity over a long period but also effectively suppresses the chlorination reaction, thereby sustaining high yields of the target products. This is because the construction of a multi-level pore structure prevents the agglomeration of Ru nanoparticles during high-temperature processes, maintaining a high dispersion of the active components. Therefore, Ru species possess excellent anti-chlorination properties. At the same time, the abundance of acidic sites promotes the cleavage of C-Cl bonds and facilitates the removal of Cl species in the form of HCl, thereby alleviating chlorine poisoning and enhancing catalyst stability.

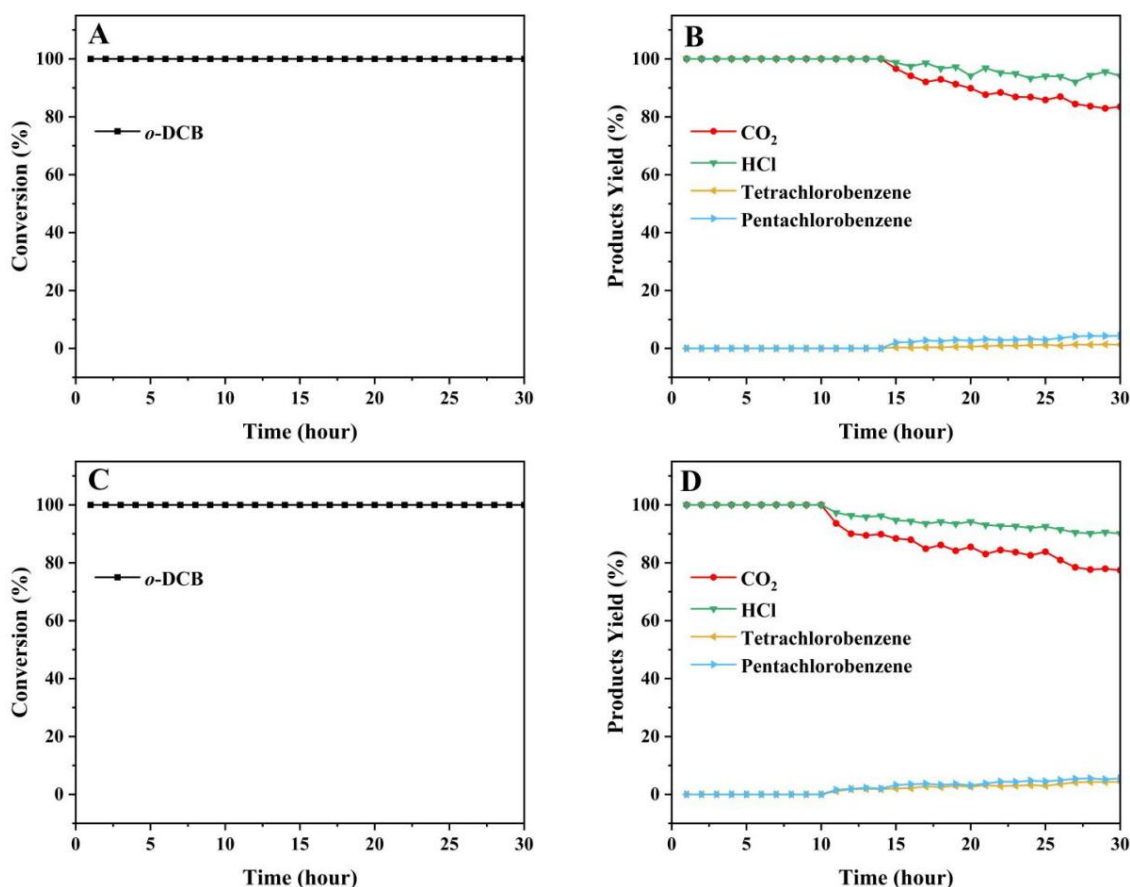


Figure 10. The long-term test of catalysts at 400 °C: (A) *o*-DCB conversion and (B) yields of products on the Ru/Beta-NaOH catalyst; (C) *o*-DCB conversion and (D) yields of products on the Ru/Beta catalyst. Conditions: 1000 ppm *o*-DCB, 10 vol.% O₂ balanced by N₂, and GHSV = ~40,000 h⁻¹.

3.4. Structure-Performance Relationship

To systematically investigate the effects of different etching strategies on the catalytic performance for the oxidation of *o*-DCB, the Ru/Beta catalyst was modified using four etchants (NaOH, Na₂CO₃, NH₄F, and HNO₃), which differ in their modification mechanisms and the corresponding effects, followed by a series of characterizations. XRD (Figure 1) revealed that the etching treatment did not alter the overall structure of the catalyst, the zeolite framework remained intact and continued to exhibit the typical BEA topological configuration. SEM (Figure 2) showed that the etching treatment did not significantly disrupt the overall morphology of the catalyst, but the surface roughness increased to varying degrees. A rough surface facilitates the exposure of active sites and the dispersion of Ru nanoparticles, thereby providing favorable conditions for optimizing catalytic performance. Among these, the surfaces of catalysts etched with Na₂CO₃ and HNO₃ were relatively smooth. Although the catalyst etched with NH₄F exhibited extremely high surface roughness, it compromised morphological integrity. Only the catalyst etched with NaOH achieved the optimal balance between roughness and integrity. Furthermore, N₂ adsorption-desorption experiments (Figure 3) and TEM (Figure 2) observation indicate that there are fundamental differences in the effects of different etchants on the pore structure of Beta zeolites. The strong desilication effect of NaOH constructed a well-developed mesoporous network within the catalyst ($V_{\text{meso}} = 0.94 \text{ cm}^3 \cdot \text{g}^{-1}$, with a pore size distribution of 2–11 nm), while retaining a certain amount of micropores ($V_{\text{micro}} = 0.23 \text{ cm}^3 \cdot \text{g}^{-1}$), thereby forming a typically hierarchical pore structure. The multilevel pore system promotes both mass transfer and shape selectivity in catalytic reactions. The good connectivity of the hierarchical pore structure and the large pore channels facilitate the diffusion of the bulky RuCl₃ precursor within the channels, while the high S_{BET} ($801 \text{ m}^2 \cdot \text{g}^{-1}$) significantly increases the number of sites for Ru species to occupy, thereby improving the dispersion of the active components. Na₂CO₃ exhibits a milder desilication effect compared to NaOH, and its etching effect on Beta zeolite is relatively weaker. Therefore, the mesopores formed by Na₂CO₃ etching are primarily concentrated in the narrow range of 2–8 nm ($V_{\text{meso}} = 0.57 \text{ cm}^3 \cdot \text{g}^{-1}$). Due to the limited etching effect, the richness and connectivity of the resulting multi-porous structure are weaker than those of the Ru/Beta-NaOH samples, which limits its ability to promote the dispersion of Ru species. Consequently, its dispersion effect is lower than that of the Ru/Beta-NaOH catalyst. Although NH₄F dealumination introduces some mesopores ($V_{\text{meso}} = 0.54 \text{ cm}^3 \cdot \text{g}^{-1}$), its S_{BET} decreases significantly ($554 \text{ m}^2 \cdot \text{g}^{-1}$), which limits the dispersion of Ru species. Al removal by HNO₃ etching results in only minimal changes to the pore structure and a small S_{BET} ($523 \text{ m}^2 \cdot \text{g}^{-1}$), which is similarly detrimental to Ru dispersion and leads to aggregation into Ru clusters. These results were verified by TEM average particle size ranking: Ru/Beta-NaOH < Ru/Beta-Na₂CO₃ < Ru/Beta < Ru/Beta-NH₄F < Ru/Beta-HNO₃. Furthermore, ²⁷Al MAS NMR analysis indicated that etching with NaOH and Na₂CO₃ effectively preserved the integrity of the framework Al, whereas etching with NH₄F and HNO₃ resulted in significant loss of framework Al. Consequently, the Ru/Beta-NaOH catalyst with a high framework Al content achieved highly dispersed Ru species (average particle size of 3–4 nm) due to its abundant anchoring sites and strong metal-support interactions. In contrast, the Ru/Beta-HNO₃ catalyst, which suffered severe loss of framework Al, featured Ru species prone to migration and agglomeration. This resulted in an increase in particle size to 10–11 nm. These findings further confirm the critical role of preserving the integrity of the framework Al in constructing highly active Ru-based catalysts.

Previous studies have confirmed that pore structure is the primary factor determining the catalytic efficiency of macromolecular chlorinated aromatics [16]. The multilevel pore structure created by etching technology significantly facilitates the diffusion of reactants, reaction intermediates, and products, thereby preventing carbon deposition caused by prolonged residence in micropores. At the same time, these multilevel pore structure exposes more active sites, thereby enhancing their accessibility. Among these, Ru/Beta-NaOH demonstrates a conversion exceeding 95% even before reaching 400 °C, thanks to its highly developed mesoporous network. This fully illustrates the essential role of pore engineering in the degradation of macromolecular pollutants. In addition, the key strength of the multilevel pore structure lies not only in alleviating the diffusion constraints on *o*-DCB molecules, but also in promoting the diffusion of larger polychlorinated byproducts within the pore channels, such as trichlorobenzene, tetrachlorobenzene, and pentachlorobenzene. To verify this effect, this study performed molecular dynamic (MD) simulations of pentachlorobenzene as the maximum-sized byproduct at 623 K, with results shown in Figure 11 and Supplementary Table S4. The results indicate that the self-diffusion coefficient (D_{self}) of pentachlorobenzene in the simulated etched mesopores is significantly greater than its D_{self} in the unetched Beta zeolite micropores, and continues to increase as the pore diameter increases. These results confirm that the mesopores formed by the etching strategy effectively promote the mass transfer of large-molecule polychlorinated byproducts within the catalyst channels, thereby facilitating their deep conversion and ultimately improving the selectivity of the target product. Moreover, in a multi-porous structure, large molecules can undergo preliminary

conversion in the mesopores and the generated small-molecule intermediates can then enter the micropores for deep oxidation. This synergy between mesopores and micropores further boosts catalytic performance and selectivity.

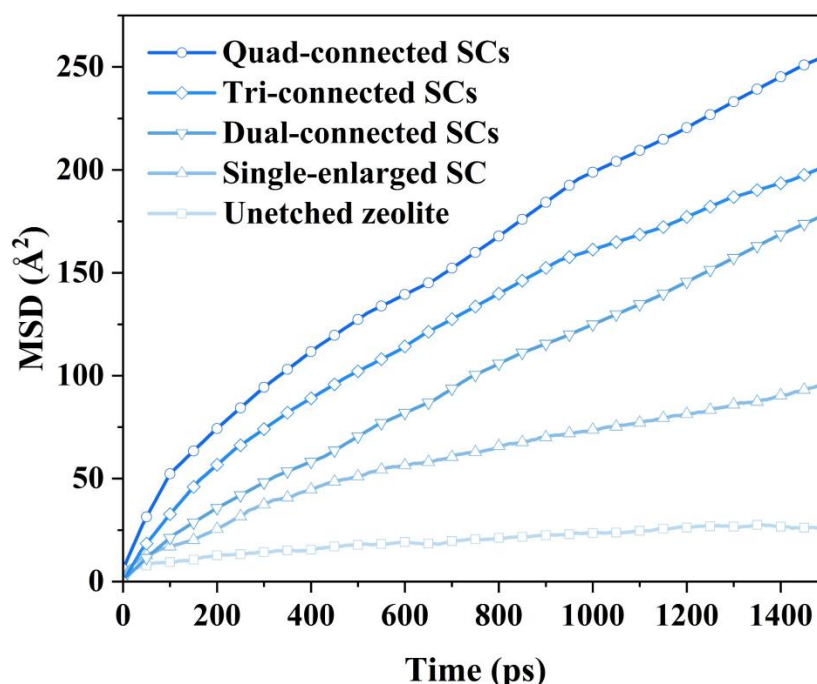


Figure 11. The MSD curves of pentachlorobenzene molecules in zeolites of varying pore sizes.

In addition, the abundance of acidic sites on the catalyst not only enhances the adsorption of *o*-DCB but also effectively guides chlorine species toward conversion to HCl, thereby improving the selectivity of the reaction pathway. Combining the NH₃-TPD results (Figure 5) and product distribution data (Figure 9), it was found that for the Ru/Beta-NaOH and Ru/Beta-Na₂CO₃ samples with abundant acidic sites, the Cl₂ yield was low and rapidly dropped to zero, while the polychlorinated benzenes yield declined sharply after 350 °C. In contrast, the Ru/Beta-NH₄F and Ru/Beta-HNO₃ samples, which are deficient in acidic sites, exhibited relatively high Cl₂ yields, with yields of polychlorinated benzenes remaining above 30% even at 400 °C. This striking contrast fully demonstrates the critical role of acidic sites in guiding the removal pathways of chlorine species. The acidity of the catalyst is also regulated by the framework Al species. The etching of NaOH and Na₂CO₃ effectively preserves the framework Al, thereby maintaining a high acid content, which is the fundamental reason for their excellent selectivity. H₂-TPR characterization (Figure 6) further revealed the patterns of changes in redox properties. The Ru/Beta-NaOH and Ru/Beta-Na₂CO₃ catalysts, which have smaller particle sizes and higher dispersion, exhibit lower reduction temperatures, highlighting their superior redox capabilities. At the same time, etching treatment regulates the distribution of surface oxygen species. The abundant defect sites and pore structures created by NaOH etching provide numerous sites for oxygen adsorption, resulting in the highest O_a ratio (Figure 7). A higher O_a content indicates stronger deep oxidation capability of the catalyst, which explains why Ru/Beta-NaOH exhibits the highest CO₂ yield and the lowest CO yield at all temperature points.

In summary, different etching techniques have influenced the pore structure, acidity, and redox properties of the catalysts, leading to variations in catalytic performance. The Ru/Beta-NaOH catalyst achieved synergistic benefits, including optimized pore channels, increased acidity, and enhanced redox performance. The refined hierarchical pore structure eliminates diffusion limitations and enhances reaction efficiency, while abundant acidic sites activate C-Cl bonds and guide the selection of HCl pathways. Furthermore, the high O_a ratio, minimal Ru particle size, and strong metal-support interactions facilitated by Al species contribute to superior redox performance. The synergy of these four factors results in optimal performance in terms of low temperature activity, target product selectivity, and undesired byproduct suppression.

4. Conclusions

Considering the modification effects of four typical etching strategies (NaOH, Na₂CO₃, NH₄F, and HNO₃) on Beta zeolite supports along with their catalytic performance in the oxidation of *o*-DCB using Ru-loaded catalysts, a comprehensive relationship was established linking etching mechanisms, structural evolution, active sites, and catalytic performance. The following key conclusions were drawn:

First, pore structure is the fundamental basis of the reaction. Different etchants possess inherently distinct effects on the regulation of the pore structure of Beta zeolites. Etching introduces mesopores with a multi-pore-size distribution, forming a hierarchical pore structure in which micropores and mesopores coexist. The construction of a multilevel pore system is a prerequisite for enhancing the catalytic efficiency and product selectivity for the chlorination of macromolecular aromatic hydrocarbons. However, it is essential to ensure the connectivity and orderliness of the pore network. Second, acidic sites play a crucial role in the catalytic process. Brønsted acid sites guide the deactivation of chlorine species via the HCl pathway. Finally, redox capacity is pivotal for deep oxidation. The adsorption oxygen content and the dispersion of Ru species jointly determine the deep oxidation capacity, and both are coordinately controlled by the pore structure and metal-support interactions.

Comparative studies have confirmed that desilication-based alkali etching (particularly NaOH etching) achieves simultaneous optimization of pore engineering and active sites by constructing a multilevel pore aperture, preserving the integrity of the aluminum framework, modulating surface acidity and enhancing redox properties. This makes it an effective etching strategy for the highly efficient catalytic oxidation of chlorinated aromatics. Furthermore, this study provides a systematic theoretical basis for the post-treatment of Ru-based zeolite catalysts aimed at the degradation of macromolecular chlorinated aromatics, establishing multidimensional catalyst design principles centered on pore-aperture optimization, acidity regulation, and surface-chemistry modulation.

Supplementary Materials

The additional data and information can be downloaded at: <https://media.sciltp.com/articles/others/2607301335218308/ESG-26050227-SI.docx>.

Author Contributions

B.X.: writing—original draft preparation, investigation, formal analysis, data curation; S.W.: writing—original draft preparation, software, visualization, formal analysis; X.G.: visualization, validation; J.J.: validation; Y.W.: methodology, validation; R.Z.: writing—review & editing, resources, project administration, methodology, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement

Not applicable.

Data Availability Statement

Data are contained within the article and supplementary materials.

Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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