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Impact of residual ions on catalyst structure and catalytic performance: A review

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ABSTRACT

Residual ions introduced during catalyst synthesis can significantly impact both the structure and performance of the catalyst. Despite their crucial role, the effects of these residual ions are frequently overlooked in catalyst design and optimization. This review systematically surveys the characteristics and sources of typical residual ions in catalytic systems, including halogen anions, acidic anions, and alkali metal cations. It also examines their impact on both the supports and active metals of supported catalysts, as well as the alterations in surface, crystal structure, and chemical states of non-supported catalysts. The effects of residual ions on the performance of these catalysts in catalytic reactions such as oxidation and hydrogenation are discussed in detail. Additionally, the influence mechanism of residual ions on the catalysts is further explored, with a focus on their promotion and inhibition roles in catalytic processes, thus providing insights for the development of more efficient and durable catalysts. A summary finally provides an outlook on future approaches to advance catalyst preparation and mitigate the adverse effects of residual ions in catalysis.

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1. Introduction

Catalysis plays a crucial role in the global economy, with widespread applications in chemical synthesis, environmental remediation, and energy conversion [1–3]. It is estimated that over 90 % of chemicals are produced through catalytic processes [4–6]. Catalysts are the heart of catalytic reactions and can significantly enhance reaction rates and selectivity by lowering the activation energy. For decades, the development of catalysts with excellent activity, selectivity, and stability has been a primary goal in the field of catalysis [7–9]. However, the design of efficient catalysts mainly focuses on engineering the active sites or supports, often ignoring the impact of residual impurities in the catalytic system.

In the practical preparation of catalysts, it is usually inevitable to have some residual ions, which can originate from the precursor salts, solvents, or other reagents used [10–12]. Typical residual ions include halogen anions, acidic anions, and alkali metal cations [13–15], and even small amounts can significantly affect the structure and performance of catalysts in various ways (Fig. 1). Specifically, residual ions can alter the structure and electronic environment of the active sites, affect the adsorption-desorption processes, or interact with reaction products, altering the overall catalytic performance. The impact of residual ions on catalytic performance is dual, with both promotive and inhibitory effects. For example, residual chloride ions can enhance catalytic performance by stabilizing specific oxidation states or promoting the dispersion of active sites [16]. Conversely, they may hinder catalytic activity through poisoning of active sites, destabilization of structures, or adverse alterations to the electronic properties of the catalyst [17]. Therefore, a comprehensive investigation into the complex effects of residual ions on catalysts is essential for the design of efficient and stable catalysts.

Previous studies primarily focused on the optimization of catalyst preparation methods, but there were few reviews on the effects of residual ions introduced during the preparation process [18,19]. This review aims to fill this gap by providing an in-depth analysis of the impact of residual ions on catalyst structure and properties. Through a review of current research, we will explore the impact of residual ions on the structure of supported and non-supported catalysts, focusing on their effects on active sites, support materials, and overall catalytic efficiency. This review will also examine the mechanisms through which residual ions interact with catalyst components, contributing to changes in catalytic

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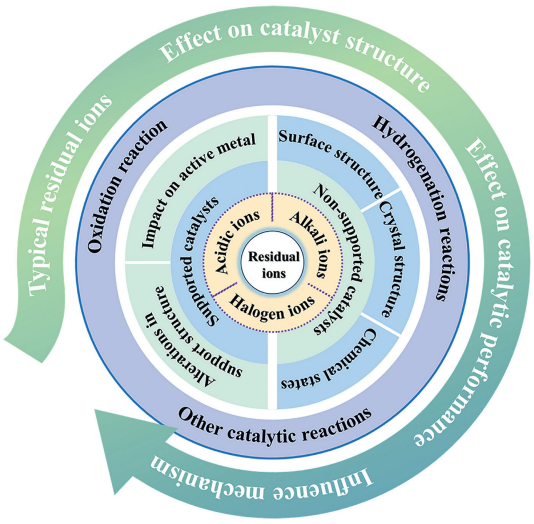


Fig. 1. Schematic diagram of the effects of typical residual ions on catalyst structure and performance.

reactions. The knowledge gained from this analysis will improve our understanding of catalyst preparation and performance and inform future research efforts aimed at reducing or controlling the impact of residual ions in catalysis.

2. Typical residual ions and their sources

Residual ions are prevalent in catalysts after synthesis, typically introduced during the catalyst preparation process. The types of residual ions are diverse, including residual halogen anions, acidic anions, and alkali metal cations. These ions interact with the catalyst in different ways and can significantly affect the overall structural integrity and chemical properties of the catalyst. The type, concentration, and distribution of these ions largely depend on the synthesis route and precursor materials employed, which govern both their initial introduction and residual presence in the catalyst. In this section, we provide a brief introduction to the characteristics and sources of typical residual ions. By understanding these aspects, the impact of residual ions on the structure and performance of catalysts can be better evaluated.

2.1. Residual halogen anions

Halogen compounds are important chemical precursors, morphology-controlling agents, and noble metal ingredients for the fabrication of catalysts [20]. However, it is important to mention here that the use of these compounds often results in residual halogen ions, such as fluoride (F^-), chloride (Cl^-), bromide (Br^-), and iodide (I^-). These ions can strongly interact with metal centers or support surfaces in the catalyst, often remaining adsorbed or incorporated into the support lattice. A summary of studies on residual halogen anions in reported catalysts is presented in Table S1 (Supporting information) [10,11,13,16,17,20–43]. Current studies on the effects of residual halogen ions in catalysts largely focus on residual Cl^-, mainly due to the widespread use of metal chlorides as precursors valued for their high solubility, reactivity, and low cost. Supported metal catalysts are typically prepared by impregnating metal chloride precursors (*e.g.*, $RuCl_3$, $HAuCl_4$, and $PtCl_4$). For example, a common preparation process of Ru/TiO_2 includes the loading process of $RuCl_3$, the filtration washing process, and the high-temperature reduction process [21]. However, subsequent calcination or washing processes often fail to completely remove Cl^-. Residual Cl^- might strongly adsorb on metal active sites or remain immobilized on the support. Additionally, Cl^- could be introduced into catalysts by immersion in chloride solutions, such as HCl, NH_4Cl, or KCl, commonly used in control experiments. Typically, the Cl^- is preferentially deposited on the support materials, especially on materials like Al_2O_3 and CeO_2, which exhibited strong adsorption of Cl^-. However, this is not a static process. During subsequent heat treatment or catalytic reactions, Cl^- often undergoes migration and transformation, a complex process that could significantly alter its distribution. Furthermore, F^- was typically introduced through fluorinated precursors or hydrofluoric acid. Due to their small ionic radius and high electronegativity, F^- tended to integrate into the crystal lattice. For instance, F^- can easily replace O^{2-} in the lattice and remain as a residual component in Mn_2O_3 catalysts prepared *via* co-precipitation using manganese fluoride as a precursor [22].

In comparison, research on residual Br^- and I^- in catalysts is relatively limited. Metal bromides and iodides are generally more expensive, less soluble, and less thermally stable, which makes them less suitable for producing uniform and stable catalysts. However, despite these limitations, residual Br^- and I^- may still play crucial roles in specific catalytic systems or under particular reaction conditions, thus warranting further investigation. For example, Chen *et al.* [23] reported that residual Br^- could originate from the modification of CuZnZr catalysts with $CuBr_2$. During high-temperature reduction, a portion of $CuBr_2$ was converted into CuBr phases and stabilized on the catalyst surface. These residual Br^- significantly affected the structure and performance of the catalyst.

2.2. Residual acidic anions

In addition to residual halogen ions, anions such as sulfate (SO_4^{2-}), nitrate (NO_3^-), carbonate (CO_3^{2-}), and acetate (CH_3COO^-) are common in catalyst preparation. It has been reported that CO_3^{2-} and CH_3COO^- are thermally unstable and decompose during calcination [44,45]. Consequently, these anions are typically absent in the final catalyst structure and have negligible effects on its properties. In contrast, SO_4^{2-} and NO_3^- are more thermally stable and can remain in the catalyst even after high-temperature calcination [46]. Among them, residual SO_4^{2-} has been extensively studied for its pronounced influence on the structural and catalytic properties of catalysts [47]. A summary of studies on residual acidic anions in reported catalysts is presented in Table S2 (Supporting information) [14,34,44–55].

Metal sulfates and nitrates are commonly used as precursors for the preparation of metal oxides. For example, Mn_2O_3 can be synthesized *via* a co-precipitation method using $Mn(NO_3)_2$ or $MnSO_4$ as a precursor [46]. While NO_3^- has negligible effects on catalytic activity, residual SO_4^{2-}, which often covers the catalyst surface, is identified as a crucial factor in catalyst deactivation. Additionally, residual SO_4^{2-} can originate from alkali metal salts, such as Na_2SO_4 [44], used for catalyst modification, or from thiourea-based electrolytes [48] employed during anodization processes. Notably, samples obtained from commercial sources may contain trace amounts of residual impurities. For instance, Chen *et al.* [49] detected small amounts of residual SO_4^{2-} on commercial TiO_2 supports and highlighted that their distinct significance was often overlooked in research. Such observations emphasize the prevalence and persistence of residual anions in catalysts. Further investigation into their effects on the structure and performance of catalysts is crucial and will be detailed in subsequent sections of this review.

2.3. Residual alkali metal cations

Compared with the above residual anions, the study of residual cations remains relatively restricted, but their impact on catalyst

structure and performance is equally significant. Current research primarily focuses on alkali metal cations, particularly sodium (Na^+) and potassium (K^+) ions [56,57]. The specific information is summarized in Table S3 (Supporting information) [12,15,56–65].

Precipitation is one of the most commonly used methods for catalyst preparation, with typical precipitants including sodium and potassium bases, such as NaOH, Na_2CO_3, KOH, or K_2CO_3. However, it is important to note that after precipitation, residual amounts of the precipitants or species derived from it might remain on the catalyst precursor, which generally alters the final properties of the desired catalyst [58]. For example, many Cu-based catalysts were often prepared using the conventional precipitation method with Na_2CO_3 or $NaHCO_3$ aqueous solutions as precipitants [59]. Residual Na^+ in the catalyst precursor can lead to variations in the physiochemical properties of the catalyst and further influence its catalytic performance. While the beneficial effects of alkali metal ions as promoters for catalyst modification have been widely studied and recognized, their role as residual ions presents a dual impact, exhibiting both promotional and inhibitory effects.

3. Effect of residual ions on the structure of catalysts

Residual ions from the preparation processes of catalyst can significantly alter the structural characteristics of catalysts, which in turn affect their performance. This section explores the impact of these residual ions on both supported and non-supported catalysts, focusing on their influence on the active metal, support structure, surface structure, crystal structure, and chemical states.

3.1. Supported catalysts

Supported catalysts are typically prepared by integrating a support material with an active metal [66]. This integration enhances the catalytic activity of the metal with the structural and functional attributes of the support, offering enhanced stability, high surface area, and tunable properties. However, residual ions can profoundly influence the structure and interaction between the metal and support. This section examines the impact of residual ions on supported catalysts, with particular focus on their influence on the active metal and the structural integrity of the support material.

3.1.1. Impact on active metal

In supported catalysts, the active metal constitutes the core of the active sites, which serve as the sites for reactant molecule adsorption and reaction. The interaction between residual ions and active metals can significantly alter their structure, potentially leading to changes in particle size, dispersion, and the electronic properties of the metal. These changes in structure can subsequently influence the reaction pathway and overall catalytic efficiency.

The impact of residual ions on metal particle size and dispersion is well-documented. A classical instance is the aggregation of Au particles during the calcination step in the presence of residual Cl^-. This agglomeration effect is especially pronounced at elevated temperatures, as gold and chloride ions readily combine to form bridges that promote particle growth upon heating [67]. Many studies have shown that the average size of Au particles in catalysts with high residual Cl^- content is large [68,69]. For example, Dobrosz *et al.* [68] synthesized Au/Mg_4Al_2 catalysts using $HAuCl_4$ as the precursor. The increase in the initial concentration of the $HAuCl_4$ solution, which brings a higher residual Cl^- content, resulted in the agglomeration of Au particles during calcination. Furthermore, Gao *et al.* [70] reported that Cl^- in the precursor could also affect the dispersion of Pd species. Pd/Al_2O_3 catalysts were prepared using $PdCl_2$ as the metal precursor. After calcination in air at 600 °C, 0.35 % residual Cl^- was still detected, which negatively affected the dispersion of Pd on the catalyst surface. Oppositely, Ito *et al.* [41] pointed out that the Cl^- derived from $PdCl_2$ precursor and added from NH_4Cl impregnation, which both contributed to the enhancement of Pd metal dispersion on the Pd/Al_2O_3 catalyst. It was found that Cl species combined with Pd species promoted the formation of small-sized Pd species and enhanced the dispersion of Pd during the process of calcination [71]. However, the smaller precious metal nanoparticles (NPs) had higher surface energy. At elevated calcination temperatures (873 K), small NPs might aggregate through the migration and combination of microcrystals, which led to the formation of larger clusters and a reduction in the dispersion of the active metals [72].

The impact of residual chloride may also vary under different heat treatment atmospheres. Fiuza *et al.* [38] investigated the effects of residual Cl^- and activation schemes on CeO_2-supported AuCu catalysts. In chlorinated catalysts, the size distribution of Au NPs broadened after both oxidative and reductive activation protocols compared to the chlorine-free catalysts. The effect was more pronounced in the case of reductive activation, which resulted in the average size of the metallic NPs doubled. Smirnova *et al.* [40] reported that for Ru/Sibunit catalysts reduced in hydrogen, the majority of the active component was present as large (50–60 nm) conglomerates. The replacement of hydrogen reduction of the Ru precursor with calcination in the argon atmosphere could prevent sintering and agglomeration of the metal particles. Therefore, the influence of residual Cl^- on metal dispersion is a complex process, typically governed by the synergistic interaction of multiple factors.

Additionally, the interaction between the metal and residual ions can lead to a shift in the electronic structure of the active metal. Residual ions on the catalyst surface can influence the chemical state of the active metal through electron attraction or charge transfer mechanisms. For example, Zhu *et al.* [20] found that residual halogen ions could adsorb on the surface of Pt-TiO_2 catalysts and form coordination bonds with Pt, which led to electron transfer from halogen ions to metallic Pt and changed the surface chemical state of Pt NPs. Similarly, Kondarides *et al.* [73] indicated that chloride species could form chemical bonds with rhodium species, leading to the stabilization of Rh^{3+} oxidation state rhodium species due to this direct chemical interaction. This oxidation state of rhodium is typically absent in catalysts without chloride, indicating that the presence of chloride species significantly altered the oxidation state and local coordination environment of rhodium species. Shi *et al.* [29] noted that residual Cl^- affected the electronic state of Pt, thereby altering the structure and activity of the catalyst. This effect was not caused by the direct accumulation of chloride ions near Pt atoms, but rather through modifications to the electronic and structural characteristics of Pt clusters. Lin *et al.* [28] demonstrated that Cl^- might coordinate palladium ions together with oxygen ions, thereby directly affecting the surface state of palladium species. Furthermore, residual ions can modulate the acidity or redox properties of active metal sites, thereby affecting the reaction selectivity of the catalyst. Huang *et al.* [30] first developed a Pt/CeO_2 catalyst with soft Lewis acid functionality, suggesting that residual Cl^- could enhance the Lewis acidity of the platinum metal center. XPS spectra of the prepared catalysts were measured to analyze the chemical state of the supported Pt species. For the catalysts containing Cl^-, Cl^- formed a chemical bond with Pt atoms (Pt-Cl), altering the electronic distribution of the Pt center, which made it more prone to accept electron pairs and exhibited stronger Lewis acidity.

In summary, residual ions, particularly chloride, profoundly impact the structure of active metals in supported catalysts. These ions can alter metal particle size, dispersion, and electronic properties, which subsequently affect the catalytic performance.

3.1.2. Alterations in support structure

The support plays a crucial role in stabilizing the dispersion of the active phase and altering its electronic state [33]. In addition to interacting with the active metal, residual ions can affect the support and significantly alter its structural integrity. These interactions can lead to changes in surface properties, pore structure, and phase composition, which can further influence the metal-support interactions. As a result, the structure or properties of the active metal may be altered.

The porous structure of the support is essential for providing a high surface area, which facilitates the dispersion of the active metal and enhances the accessibility of reactants to active sites. Residual ions, particularly Na^+ [59], $SO_4^{2-}$and NO_3^- [44], can interact with the surface of the support and alter its pore structure. For instance, in Cu-CeO_2-Al_2O_3 catalysts prepared by co-precipitation, residual Na^+ was present in the form of Na_2CO_3, which covered the catalyst surface [59]. This coverage led to the sintering of the support matrix and clogging of the catalyst pores, resulting in a compact surface. The catalyst displayed an aggregated morphology of the corresponding matrix particles after the removal of residual Na^+. In some cases, residual ions on the surface of the support can significantly alter the acidity of the support. Shkurenok *et al*. [55] demonstrated that in Pt-containing WO_3/ZrO_2 catalysts, SO_4^{2-} from the $ZrSO_4$ precursor increased the number of strong acid sites on the synthesized support, thereby enhancing the acidity of the catalyst. On the other hand, the positive effect of residual Cl^- on the surface acidity of the support in Pt/Al_2O_3 catalysts had also been demonstrated by Pauils *et al*. [36]. NH_3-TPD results indicated that the presence of residual Cl^- led to a slight increase in the amount of NH_3 desorbed from the surface, which corresponded to an increase in surface acid sites. This effect was attributed to the strong affinity of the alumina support for chloride ions, resulting in the deposition of chlorides on the support and the formation of a more acidic catalyst [74]. Oenema *et al*. [75] observed a similar effect in Pt/Zeolite Y/γ-Al_2O_3 catalysts but found that Cl^- coordinated with γ-Al_2O_3, which might lead to the formation of an $AlCl_3$ phase on the surface, which is a strong Lewis acid. Moreover, the catalysts with higher chlorine content exhibited enhanced acidity.

The interaction of residual ions with the support material could also affect the phase composition and structural stability of the support. Metal oxide supports, such as CeO_2, were prone to phase transitions when exposed to specific ions. It was well known that chlorine had a strong interaction with ceria [32]. Thus, catalysts derived from chlorine-containing precursors tended to incorporate significant amounts of Cl^- into the support, and complete removal was difficult due to the formation of CeOCl, which could only be decomposed by an aging treatment. Kepinski and Okal [76] investigated the formation mechanism of CeOCl in Pd/CeO_2 catalysts prepared using $PdCl_2$ as a precursor. These authors found that Cl^- remained strongly chemisorbed on ceria at low reduction temperatures. However, an increase in the reduction temperature to 673 K resulted in the progressive incorporation of Cl^- into the oxygen vacancies (OVs) of the support and led to the growth of these CeOCl crystallites, as confirmed by X-ray diffraction (XRD). Moreover, in addition to the growth of the CeOCl crystals, an important loss of the catalyst surface area was observed. This fact indicated that the incorporation of the Cl^- induced changes in the textural, structural, and chemical properties of the support. The blockage of surface Ce^{3+}-coupled OV sites by CeOCl consequently reduced the redox performance of the support [31]. Furthermore, the presence of chloride ions could hinder the formation of hydroxyl groups and carbonate or carboxylate species on the ceria surface, thereby affecting its surface chemistry [77]. Additionally, the presence of residual Na^+ also played a significant role in the crystal structure of the support. For example, Zhao *et al*. [63] revealed the significant role of residual Na^+ in the support of aluminum-rich Cu-exchanged SSZ-13 zeolite. Residual Na^+ could partially stabilize the surface and crystal structure of Cu-SSZ-13, but excessive amounts led to structural degradation and a reduction in the high-temperature stability of the catalyst.

The various effects of residual ions on the support structure often further influence metal-support interactions. For example, the CeOCl species formed by the reaction of Cl^- with CeO_2 created obstacles on the catalyst surface, preventing the uniform distribution of active metal species and thereby impacting their dispersion [78]. On the other hand, the presence of residual ions could also influence the nature of the metal-support bond, with consequences for the stability and reactivity of the catalyst. Liu *et al*. [52] demonstrated that SO_4^{2-} anchored to the NiMo/γ-Al_2O_3 catalyst surface weakened the metal-support interaction and hindered the $NiAl_2O_4$ formation due to its thermal stability and strong interaction with Al_2O_3, thereby facilitating both the sulfidation of Mo species and the decoration of Ni atoms and generating more Ni-Mo-S active sites. In addition, the aggregation and growth of the active phases were also effectively inhibited by these anchored SO_4^{2-}, thus guaranteeing a catalyst with high metal dispersion and good stability.

3.2. Non-supported catalysts

Non-supported catalysts, typically composed of metal oxides, composite oxides, or other solid materials, are of significant importance in various catalytic processes due to their high intrinsic activity and stability. The structural integrity and chemical properties of these catalysts are critical to their catalytic performance, and the residual ions introduced during the preparation can profoundly affect these characteristics. The effects of residual ions on the structure of non-supported catalysts are investigated in this section, with a focus on their surface structure, crystal structure, and chemical states.

3.2.1. Surface structure

The surface structure of non-supported catalysts is essential for catalytic performance. During synthesis or activation, residual ions can interact with the catalyst surface, which can modify the surface morphology, roughness, and active site exposure of these catalysts. For example, García-López *et al*. [24] revealed that during the synthesis of shape-controlled TiO_2 materials, an increase in the F^- content resulted in a higher percentage of exposed {001} facets on the TiO_2 surface. However, calcination at 500 °C was used to remove surface F^-, which resulted in a decrease in the number of exposed {001} facets and a transformation of the original plate-like shape of nanocrystals to a more isotropic one. These observations suggested that the residual F^- played a crucial role in stabilizing the {001} facet-enriched anatase NPs. In some cases, residual ions could also affect the surface roughness of catalysts. Liao *et al*. [48] prepared a NiFe (oxy)hydroxide catalyst containing residual SO_4^{2-}($NF\text{-}S_{0.15}$) through an electrochemical anodization procedure. As shown in Figs. 2a-c, $NF\text{-}S_{0.15}$ exhibited a rough surface with a homogeneous silkworm-like appearance and consisted of curly nanosheets with a thickness of about 5 nm. This surface morphology differed from the smooth surface of the unmodified NiFe foam and was attributed to the presence of residual SO_4^{2-}.

Furthermore, the residual anions, specifically SO_4^{2-} and Cl^-, could influence the specific surface area and porosity of transition metal oxides [34,35,45]. Zhang and co-workers [45] reported that the residual SO_4^{2-} in Mn_2O_3 formed sulfate clusters after thermal aging. They indicated that this phenomenon did not alter the morphology of the sample but blocked active sites, hindering the transport of reactants and lattice oxygen. Samples containing residual Cl^- showed more severe sintering, likely due to the acceleration of particle growth by Cl^-, which resulted in a decrease in specific

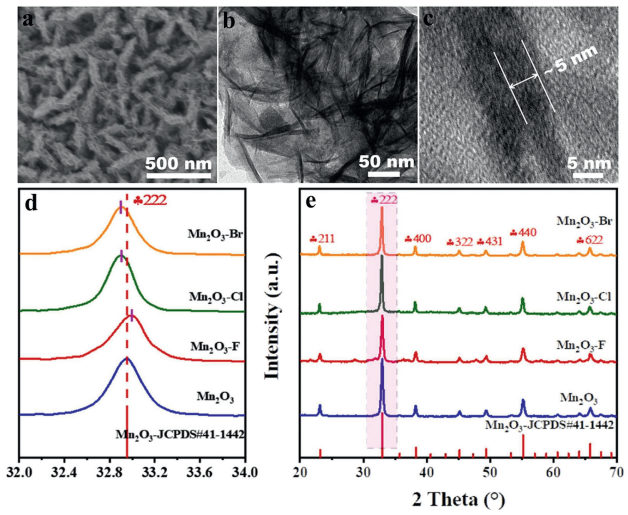


Fig. 2. (a) Scanning electron microscope (SEM), (b) transmission electron microscopy (TEM), and (c) high-resolution TEM images of NF-S0.15. Copied with permission [48]. Copyright 2021, Wiley. (d, e) XRD patterns of pristine Mn_2O_3 and Mn_2O_3 doped with F, Cl, and Br. Copied with permission [22]. Copyright 2023, Elsevier.

surface area and pore volume. Wu *et al.* [34] suggested that the removal of adsorbed SO_4^{2-} from MnO_2 catalysts (effectively achieved through quenching) exposed more active sites and increased the specific surface area.

3.2.2. Crystal structure

The crystal structure of non-supported catalysts is another aspect sensitive to the presence of residual ions. Residual ions, particularly with different ion radiuses or charges in comparison to the host lattice ions, can be incorporated into the crystal lattice during synthesis, which can induce lattice distortions and modify lattice parameters. Yu *et al.* [22] indicated that residual halogen ions doped into the crystal lattice significantly affect the crystal structure of Mn_2O_3 catalysts. As shown in Figs. 2d and e, XRD analysis revealed that the F^- dopant caused a positive shift in the {222} plane diffraction peak, indicating a shrank lattice spacing. In contrast, Cl^- and Br^- dopants resulted in a slight negative shift, suggesting the lattice spacings were widened. These changes highlighted the lattice contraction induced by F^- and the expansion aroused by Cl^- and Br^-. On the other hand, residual Na^+ incorporated in catalysts could also induce lattice distortion. Chai *et al.* [79] revealed that residual Na^+ could be partially inserted into the Co_3O_4 spinel lattice, which induced the lattice expansion and distortion. This distortion could be explained in terms of the difference in ionic radius between Co^{2+}, Co^{3+}, and Na^+. Moreover, a smaller crystallite size of the Co_3O_4 catalysts was exhibited due to the crystallization inhibited by the introduction of sodium. Significantly, catalysts with high residual Na^+ content showed the greatest specific surface area, pore volume, and average pore size, which could be attributed to the improvement in textural properties caused by the distortion of the Co_3O_4 spinel lattice. It indicated that the transformation of crystal structure often led to variations in surface structure.

Furthermore, residual ions can stabilize or destabilize specific crystalline phases, particularly under extreme conditions such as high temperatures or oxidative environments. As revealed by Zhao *et al.* [63], an appropriate amount of residual Na^+ could stabilize the framework Al in Al-rich SSZ-13 zeolites during high-temperature calcination to preserve long-range order. However, excessive Na^+ led to the degradation of the crystal structure, particularly after high-temperature aging. Liu *et al.* [51] suggested that the type of anion ligand in the Al precursor played a crucial role in the phase composition of the final AlF_3 catalyst. The catalyst prepared with $Al_2(SO_4)_3{\cdot}18H_2O$ exhibited a unique crystal structure containing α-AlF_3, β-AlF_3, and θ-AlF_3 phases, in contrast to catalysts prepared with $Al(NO_3)_3{\cdot}9H_2O$ and $AlCl_3{\cdot}6H_2O$, which predominantly showed the α-AlF_3 phase. It was attributed to the residual SO_4^{2-} ions and the decomposition of Al-OH groups during the carbonization and fluorination processes, which both inhibited the transition of crystal structures from β-AlF_3 to α-AlF_3.

3.2.3. Chemical states

In the previous section, we discussed that the incorporation of residual ions into the lattice of metal oxides could induce significant changes in the crystal structure. Indeed, this process was often accompanied by alterations in the chemical states of active components, which were crucial determinants of their catalytic activity. It is well-known that transition metals have many valence states. In the case of Mn_2O_3, the strong redox couples like Mn^{3+}/Mn^{2+} and Mn^{4+}/Mn^{3+} exposed on the surface play a critical role in catalytic oxidation reactions. When O^{2-} in Mn_2O_3 is replaced by F^-, electron density around Mn decreases due to the high electronegativity of F^-, leading to an increased proportion of Mn^{4+} and Mn^{2+}species. In contrast, Cl^- and Br^- dopants result in a decrease in Mn^{4+} and an increase in Mn^{3+} [22]. Moreover, Choya *et al.* [58] demonstrated that residual Na^+ affected the chemical state of Co_3O_4 catalysts. Na^+ acted as strong Lewis sites, transferring electrons to cobalt cations and increasing the electron density of oxygen anions. This interaction weakened the Co-O bond and effectively reduced the overall oxidation state. Catalysts with residual Na^+ showed a lower Co^{3+}/Co^{2+} molar ratio.

4. Effect of residual ions on the performance of catalysts

The catalytic performance of catalysts depends on the properties of the catalytically active sites and their accessibility to reactants [80,81]. Residual ions can interact with the active sites of catalysts, alter their surface properties, or trigger side reactions, thereby affecting catalytic performance in various reactions, particularly in terms of activity, selectivity, and long-term stability. This section explored the influence of residual ions on catalytic performance in oxidation reactions, hydrogenation reactions, and other catalytic processes, based on the available data.

4.1. Oxidation reactions

4.1.1. VOCs oxidation

Catalytic oxidation is widely recognized as one of the most promising and economical techniques to remove volatile organic compounds (VOCs) [82,83]. The oxidation process typically involves complex reaction pathways sensitive to catalyst surface characteristics. Residual ions can affect the efficiency of VOC oxidation by modifying active sites or altering adsorption properties. Among the various catalysts used for VOC oxidation, supported platinum group materials (PGMs) and transition metal oxides (Mn, Ce, Co, Cu, and Ni, etc.) have demonstrated the highest efficiency for VOC elimination [84–87]. Therefore, it is crucial to investigate the effect of residual ions on the performance of these catalysts in VOC catalytic oxidation to optimize catalyst design and improve oxidation efficiency.

Toluene, a representative VOC, has been studied to evaluate the effect of different residual ions on the catalytic degradation performance of manganese oxides. Wu *et al.* [34] investigated the poisoning effect of sulfate residues on MnO_2 catalysts used for toluene catalytic combustion. After water washing, the sulfur content in sulfate-derived MnO_2-SO_4 decreased and the temperature required for 50 % toluene conversion (T_{50}) dropped from 235 °C to 212 °C.

These findings indicated that adsorbed sulfates deactivated MnO_2 catalysts and reduced their catalytic performance for toluene oxidation. Yu *et al*. [46] synthesized Mn_2O_3 catalysts (Mn_2O_3-A, where A = Cl^-, SO_4^{2-}, or NO_3^-) using various manganese precursors and evaluated their performance in the photothermal degradation of toluene. The activity of Mn_2O_3 often declined as residual anions obstructed the Mn^{4+}/Mn^{3+}active sites, covered the OVs, and cubed the generation of active oxygen species (O_2^-, O^-). Further studies revealed that residual anions prevented the deep oxidation of intermediates on Mn_2O_3, disrupted the reaction pathway, and reduced toluene mineralization. The extent of their impact followed the order: SO_4^{2-} > Cl^- > NO_3^-. Additionally, the influence of residual halogen ions on the photothermal catalytic oxidation of toluene over Mn_2O_3 was also investigated [22]. F^- could attract the shared electrons from Mn to itself, which activated Mn_2O_3 and promoted the generation of abundant OVs. The final catalytic efficiency in the detoxification of toluene by converting it to CO_2 and H_2O was significantly enhanced, while Cl^- and Br^- exerted a negative influence. However, the percentage of toluene removal decreased because excessive F^- could cover and block the active sites implanted in Mn_2O_3. The toluene degradation efficiency was 99 %, and the degree of mineralization was high up to 95.8 % with the optimal Mn_2O_3-F (0.03 mol in the precursor).

In addition to manganese oxides, cobalt-based catalysts have also been studied to understand the influence of residual Na^+ on catalytic oxidation performance. Zhang *et al*. [56] prepared Co_3O_4 catalysts with varying Na^+ residues using a carbonate precipitation method under different pH conditions. Among these, the Co-9.5 catalyst synthesized at pH 9.5, exhibited the highest Na content (0.60 wt%) and demonstrated superior performance in toluene oxidation. However, this catalyst showed the lowest activity in propane oxidation. Their findings suggested that the enhanced toluene oxidation efficiency of Co-9.5 could be attributed to its abundant OVs, which played a critical role in facilitating the reaction. Notably, the residual Na^+ had minimal influence on the oxidation of toluene but significantly inhibited propane oxidation, which highlighted the complex and reaction-specific effects of residual ions in catalytic processes.

PGMs are highly favored in VOC catalytic oxidation due to their exceptional ability to activate C–H bonds [88]. The influence of residual ions on the performance of these catalysts has also been extensively studied. Nie *et al*. [89] reported that fluoride ions adsorbed on the surface of Pt NPs suppressed the activity of noble metal-supported catalysts for HCHO oxidation and could even lead to complete deactivation. Similarly, Zhu *et al*. [20] compared the catalytic performance of Pt-TiO_2 catalysts with and without halogen residues in formaldehyde oxidation. Their findings revealed that halogen ions inhibited the adsorption and activation of oxygen on the surface of Pt NPs, resulting in reduced catalytic activity for formaldehyde oxidation. Our research group investigated the impact of residual chlorine on the catalytic performance of Pd@ZrO_2 in degrading a range of VOCs [26]. Pd@ZrO_2 catalysts were synthesized using an *in-situ* grown Zr-based metal-organic framework (MOF) as a sacrificial template. Residual Cl^- from the Zr-MOF coordinated with atomically dispersed Pd during the pyrolysis process, forming Pd_1-Cl species. Simultaneously, abundant OVs were generated, which enhanced the adsorption and activation of gaseous oxygen, thereby accelerating the degradation of VOCs such as benzene, toluene, and xylene. Notably, in the presence of dichloromethane (DCM), the formation of Pd_1-Cl species inhibited the adsorption of DCM, releasing more active sites for the adsorption of toluene and its intermediates. It indicated that the residual Cl species could both contribute to the catalytic activity of Pd@ZrO_2 and improve its chlorine resistance. However, a separate study we conducted [25] found that residual Cl species originated from the $ZrCl_4$ metal precursor participated in the VOC degradation reaction and modified the reaction pathways, leading to the production of various chlorine-containing byproducts, even the hypertoxicity dioxin precursor, dichlorobenzene. This observation underscored a critical shift in reaction selectivity because the catalyst degraded the target VOCs as well as generated undesirable and potentially hazardous chlorinated compounds.

4.1.2. CO oxidation

CO oxidation is a commonly used probed reaction to evaluate the catalytic activity and stability of various catalysts because of its simplicity [90]. Despite the extensive research, the impact of residual ions on catalytic performance in CO oxidation remains a topic of continuous debate. However, the negative effect of residual Cl^- on the catalytic performance of various catalysts in CO oxidation has been well established. The extent of this impact varies depending on the specific catalyst used. Li *et al*. [35] reported the impact of residual Cl^- on the CO oxidation reaction over Co_3O_4. In their study, the catalytic activity of cobalt chloride-derived samples was significantly enhanced after water washing, with the T_{50} (temperature for 50 % conversion) dropping from 176 °C to 108 °C, even surpassing the Cl-free samples. Gracia *et al*. [91] investigated the influence of Cl^- on Pt-supported catalysts during CO oxidation. The results demonstrated that the Cl-free catalyst exhibited an activity approximately 10 times higher than that of the Cl-containing catalyst. According to Oh *et al*. [69], for the Au/Al_2O_3 catalyst, the CO oxidation activity of the acetate-derived catalyst was found to be nearly 30 times higher than that of the chloride-derived catalyst. The addition of chloride with a Cl/Au atom ratio of 0.1 could reduce the activity approximately by half [92].

Further studies on gold catalysts have reported the dual role of Cl^- in the inhibition of CO catalytic oxidation activity: it promotes the agglomeration of Au particles and poisons the active sites [91]. According to the previous literature, highly active catalysts typically contained small Au particles, whereas catalysts with high residual Cl^- contents tended to feature larger Au particles. This dual effect has been observed in Au/Al_2O_3 [69], Au/CeO_2 [67], and Au/$Ce_{1-x}Zr_xO_2$ [33] catalysts used for CO oxidation, where the removal of Cl^- by the wash treatment hindered the sintering process and enhanced the catalytic activity of the studied systems. Furthermore, Fiuza *et al*. [38] reported that metal-phase sintering induced by the presence of chlorides prevents the complete CO conversion over the bimetallic AuCu/CeO_2 catalyst, even at 300 °C. Such phenomenon occurred though Cu/CuO_x species were known to enhance the catalytic activity of Au-supported catalysts in CO oxidation and improve their resistance to sintering. The detrimental effect of chloride was primarily attributed to the poisoning of the interface Au-CuO_x-CeO_2 species, which was considered the most active site in the AuCu-CeO_2 catalyst for CO oxidation.

4.1.3. Methane oxidation

Compared with other alkanes, the hydrocarbon methane is the most difficult to oxidize and requires much higher temperatures for oxidation. Pd catalysts are widely recognized to be active for methane combustion. However, residual ions could affect the activity of PdO species in Pd-based catalysts, which served as active sites for methane catalytic combustion. Roth *et al*. [39] reported that residual Cl^- significantly lowered the catalytic performance of Pd/Al_2O_3 catalysts in methane oxidation, primarily by deactivating the PdO active sites. Catalysts prepared from chlorine-containing precursors exhibited high levels of residual chlorine, which strongly inhibited methane conversion by blocking crucial surface active sites involved in the reaction. While chloride-free catalysts inherently showed higher activity, under high-temperature reaction conditions (≥600 °C), residual chlorine in chlorine-containing catalysts could be removed as HCl, which ultimately restored the catalytic activity to levels comparable to

those of chloride-free catalysts. Furthermore, it was demonstrated that a mixture of Pd metal and PdO provided much higher activity for methane combustion compared to dispersed or agglomerated PdO [93]. Moderate reducibility of PdO and high oxygen exchange activity contributed to improved methane conversion. Lin *et al.* [28] developed $Pd/TiO_2/Al_2O_3$ catalysts and investigated the impact of surface residual Cl^- on their catalytic performance in the low-temperature complete oxidation of methane. Chloride ions, which coordinated with oxygen ions and palladium, modified the thermal properties of the supported palladium. Catalysts with surface chloride ions exhibited higher reduction temperatures for palladium species and increased onset temperatures for oxygen isotopic exchange reactions, resulting in lower activity in complete methane oxidation.

Additionally, Co_3O_4 catalysts are also applied for methane catalytic combustion. Zheng *et al.* [54] demonstrated that residual SO_4^{2-} impurities could cover the surface active sites, reduce the concentration of surface-adsorbed active oxygen, and impair oxygen mobility, which decreased catalytic performance. It was further confirmed by methane combustion tests. Specifically, the presence of residual SO_4^{2-} on Co_3O_4 reduced the methane conversion rate at 318 °C from 50 % to 16 %.

4.2. Hydrogenation reactions

4.2.1. CO/CO_2 hydrogenation

The catalytic hydrogenation of CO/CO_2 into valued chemicals is a promising strategy to address challenges in energy, environment, and climate change [94,95]. There are various products for CO/CO_2 hydrogenation, including CH_4, CH_3OH, olefins, and hydrocarbons, *etc.* The significant influence of residual ions on the performance and product distribution in catalytic CO/CO_2 hydrogenation has been demonstrated.

Fischer-Tropsch (FT) synthesis is one of the most common routes for CO hydrogenation catalysis. Currently, contradictory results regarding the effect of residual Cl^- on the performance of FT catalysts have been disclosed. Research by Ojeda *et al.* [96] showed that residual Cl^- on Rh/SiO_2 catalysts had no influence on reaction activity or selectivity towards the major product families. However, they led to a lower 1-olefin/n-paraffin ratio. Hydrogen temperature-programmed desorption (TPD) studies indicated that the presence of residual Cl^- promoted hydrogen spillover. The spilled-over species subsequently created active sites on the silica surface, where olefins could be hydrogenated to the corresponding kinds of paraffin. González-Carballo *et al.* [97] reported that the addition of Cl^- to $Ru/\gamma\text{-}Al_2O_3$ catalysts enhanced the initial CO conversion rate, which increased with the Cl^- concentration in the catalyst. However, under steady-state conditions, all catalysts exhibited similar FT yields, regardless of their initial amount of Cl^-. They explained that the interactions between Cl^- and Ru NPs stabilized certain $Ru^{\delta+}$-CO species, which improved CO conversion and hydrocarbon production. Nevertheless, these $Ru^{\delta+}$-CO species were unstable under reaction conditions, leading to catalyst deactivation as the reaction progressed, which resulted in a decrease in both CO conversion and hydrocarbon yield. Ma *et al.* [98] found that the KCl exhibited a low poisoning effect on iron and cobalt catalysts and slightly altered their selectivity. Notably, residual K^+ and Cl^- played contrary roles in changing hydrocarbon selectivity. For instance, K^+ enhanced CO adsorption and dissociation and promoted chain growth, while Cl^- inhibited CO dissociation and suppressed chain growth. K^+ was typically recognized as a basic promoter to boost chain growth probability and olefin selectivity, thereby enhancing the catalytic activity in FT synthesis [64]. Similarly, Gonzalo-Chacón *et al.* [99] reported that the Cl^- traces neutralized the effect of the potassium promoter on Ru-based catalysts during the FT reaction. These findings highlighted the complexity of the FT reaction mechanism and underscored the challenges that remained in understanding the impact of residual ions on the performance of FT catalysts.

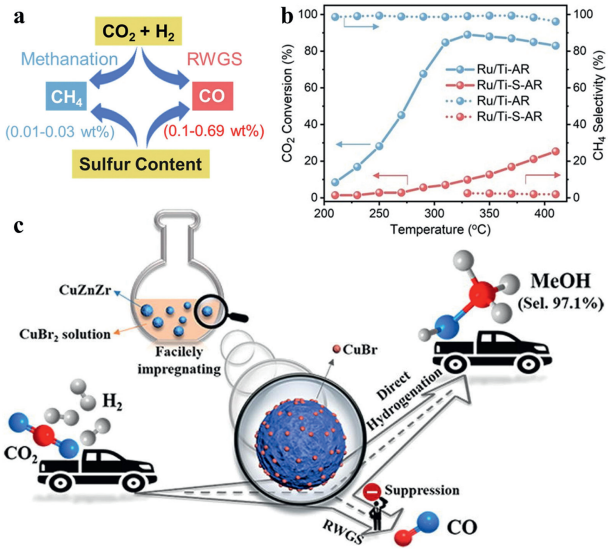


Fig. 3. (a) The products and sulfur content comparison on the different sets of Ru/TiO_2 catalysts for CO_2 hydrogenation. (b) Temperature-dependent CO_2 conversion and CH_4 selectivity of Ru/TiO_2 catalysts with or without SO_4^{2-}. Copied with permission [49]. Copyright 2024, Springer Nature. (c) Schematic diagram of CO_2 hydrogenation process over $CuZnZr/CuBr_2$ catalyst. Copied with permission [23]. Copyright 2020, Elsevier.

Numerous studies have reported the detrimental effects of Cl^- in CO_2 hydrogenation. For instance, Wen *et al.* [100] observed that Ni/TiO_2 catalysts prepared from Cl-containing Ni precursors exhibited poor catalytic activity in CO_2 hydrogenation, which was attributed to the poisoning effect of Cl^- for the catalytic system. Shimoda *et al.* [27] demonstrated that Cl^- on the Ni/TiO_2 catalyst surface inhibited the CO_2 methanation and the reverse water-gas shift reaction, thus enhancing the CO-selective methanation (CO-SMET) process during the CO/CO_2 reaction. Crawford *et al.* [101] reported that chloride contamination, owed to $RuCl_3$ precursor, significantly reduced the CO_2 methanation activity of Ru/TiO_2 catalysts. Cl^- blocked active sites on Ru that were directly involved in CO_2 hydrogenation, thereby reducing the adsorption and dissociation of CO_2 and H_2, which were critical steps in the methanation process. Experimental results showed that removing chloride contamination through an aqueous ammonia wash significantly enhanced CH_4 production. The washed catalyst displayed a 4.5-fold increase in methanation activity, particularly at lower temperatures (~225 °C). This improvement diminished at higher temperatures, indicating that the inhibitory effect of chloride was temperature-dependent.

The selectivity of Ru-based catalysts could be significantly altered by Cl^- through the inhibition of CO_2 hydrogenation [102]. Zhang *et al.* [21] investigated the chloride poisoning effect on Ru/TiO_2 catalysts and revealed its impact on CO_2 hydrogenation selectivity. The catalyst with the highest chloride content exhibited the highest CO selectivity, while a decrease in chloride content (with increased washing volume) led to a higher CH_4 selectivity. With the chloride content increased, the adsorption of CO on the catalyst surface significantly weakened, which limited the further hydrogenation of CO to CH_4 and resulted in a higher CO selectivity. Similarly, Chen *et al.* [49] demonstrated that even trace residual sulfates (0.1–0.69 wt%) on Ru/TiO_2 catalysts could completely shift the CO_2 reduction pathway at atmospheric pressure from methanation to the reverse water gas shift (RWGS) reaction (Figs. 3a and

b). This behavior closely resembled the impact of residual chloride. Additionally, the influence of residual Br^- on catalyst selectivity in CO_2 hydrogenation to methanol has also been reported. Chen *et al.* [23] demonstrated that residual Br on CuZnZr catalysts stabilized as a CuBr phase on the catalyst surface. As shown in Fig. 3c, this stabilization significantly suppressed the RWGS activity on the Cu surface, thereby enabling high methanol selectivity (97.1 %).

4.2.2. Hydrogenation of unsaturated compounds

The impact of residual Cl^- on catalytic performance in the hydrogenation of unsaturated compounds, such as aromatic compounds and carbonyl compounds, has been reported. For example, Ito *et al.* [41] investigated the effect of residual Cl^- on catalytic activity in the hydrogenation of naphthalene over Pd/Al_2O_3 catalysts. Trace residual Cl^- enhanced the acidity of OH groups on the Al_2O_3 surface and promoted the adsorption of naphthalene, thereby increasing the activity. Otomo *et al.* [42] showed that residual Cl^- acts as a poison for Co/Al_2O_3 catalysts in ketone hydrogenation but promoted aldehyde hydrogenation. Besides, Cl^- has been shown to positively influence the catalytic selectivity for hydrogenating carbonyl bonds to unsaturated alcohols [42,103]. Bachiller-Baeza *et al.* [103] synthesized graphite-supported Pt and Ru catalysts from metal chloride precursors for the gas-phase hydrogenation of crotonaldehyde. The reaction predominantly produced butyraldehyde and crotyl alcohol. Trace chloride residues enhanced the hydrogenation of the carbonyl group and increased the selectivity towards crotyl alcohol, while excessive chloride residues had the opposite effect. However, Echeverri *et al.* [37] reported that $Ru\text{-}Sn/Al_2O_3$ bimetallic catalysts prepared from chloride-containing precursors exhibited lower selectivity for unsaturated alcohols in the hydrogenation of methyl oleate compared to chloride-free catalysts. The most selective catalyst, with a selectivity of 74 % and a methyl oleate conversion of 75 %, was obtained by removing Cl^- *via* $NaBH_4$ reduction. Further analysis explained that residual Cl^- might partially inhibit the formation and dispersion of Ru-Sn species, which were crucial for achieving higher alcohol selectivity and reducing ester exchange reaction rates.

Except for Cl^-, the impact of residual Na^+ on the performance of hydrogenation catalysts for unsaturated compounds has also been documented. Yu *et al.* [59] studied the impact of residual Na^+ in the form of Na_2CO_3 on the gas-phase hydrogenation of maleic anhydride catalyzed by $Cu\text{-}CeO_2\text{-}Al_2O_3$. The results showed that Na_2CO_3 covered the active sites on the catalyst surface, which caused a reduction in both activity and selectivity. This negative effect intensified with increasing Na^+ content. In contrast, Huang *et al.* [60] investigated the influence of residual Na^+ on the catalytic performance of CuO/SiO_2 in the hydrogenolysis of glycerol to produce 1,2-propanediol. While they also observed a general decrease in conversion and selectivity with higher sodium content, the leaching of Na^+ from the catalyst surface, as a basic, slightly promoted the catalytic activity. Moreover, this leaching delayed the deactivation of active copper species, reducing the overall catalyst deactivation rate. As a consequence, they concluded that an optimal amount of sodium was required to achieve both high catalytic activity and good stability in CuO/SiO_2 catalysts.

4.2.3. Other hydrogenation reactions

In addition to the effect on catalytic performance in the hydrogenation reactions mentioned above, their significant role in ammonia synthesis has also been reported. Lin *et al.* [43] found that residual or added Cl^- negatively affected the Ru/Al_2O_3 ammonia synthesis catalyst. With a comparable amount of residual Cl^-, the catalysts with Cl^- derived from the $RuCl_3$ precursor exhibited much lower catalytic activity than those prepared by impregnation with HCl, as Cl^- would first adsorb on alumina surface when chlorine-free Ru catalysts were impregnated with HCl solution. It was also noted that Cl^- did not impact the size of the resultant metal NPs and that the reduced activity was caused by the blockage of hydrogen adsorption sites. However, Smirnova *et al.* [40] proposed that the activity of Ru-Ba/Sibunit catalysts depended on the dispersion of Ru and the residual chloride content. The presence of Cl^- led to the aggregation of Ru particles during thermal treatment, which resulted in reduced dispersion and a significant decline in ammonia synthesis activity.

In addition, the catalytic performance of NiMo catalysts in hydrodesulfurization (HDS) reactions was strongly influenced by the residual ions in the support material. Ortega-Domínguez *et al.* [61] demonstrated that the residual Na^+ content in TiO_2 nanotubes played a crucial role in dibenzothiophene hydrodesulfurization (DBT-HDS). High Na^+ content led to a reduction in catalytic activity and an enhancement in selectivity towards the direct desulfurization pathway due to the formation of less active sodium molybdate species and a higher number of coordinatively unsaturated sites. Conversely, catalysts with low Na^+ content exhibited enhanced hydrogenation ability and higher overall activity due to the ease of reduction of dispersed octahedral Mo oxide species and the predominance of fully sulfided MoS_2 phases, which were more conducive to both hydrogenolysis and hydrogenation routes of HDS. Besides, Liu *et al.* [52] demonstrated that residual SO_4^{2-} ions anchored on the Al_2O_3 surface significantly improved the DBT-HDS performance of $NiMo/Al_2O_3$, achieving a conversion rate of approximately 90 % at 280 °C. They suggested that SO_4^{2-} weakened the metal-support interaction, promoting the sulfurization of Mo and the formation of more Ni-Mo-S active sites.

4.3. Other catalytic reactions

Residual ions have also been reported to affect a variety of other catalytic reactions except for the oxidation and hydrogenation above. However, the relevant research in these fields remains limited, and further exploration in the future would be valuable. Liao *et al.* [48] revealed the dual role of residual SO_4^{2-} in the enhancement of oxygen evolution reaction (OER) performance. SO_4^{2-} enhanced the OER activity of NiFe (oxy)hydroxide by accelerating the electrochemical reconstruction of precursor catalyst and stabilizing the OOH* intermediate during the OER process. It was found that the OER activity was enhanced with the concentration of SO_4^{2-} and the optimal concentration of SO_4^{2-} was around 0.1 mol/L, where the catalyst exhibited the lowest charge transfer resistance. As a result, the charge transfer rate during the OER process was faster, which contributed positively to achieving higher OER activity. Huang *et al.* [30] reported that Pt/CeO_2 with residual Cl^- as a soft Lewis acids catalyst could achieve to highly efficient isomerization of allylic esters. Residual Cl^- enhanced the Lewis acidity of the Pt metal center, thereby improving the catalytic activity. The reaction could be achieved under solvent-free conditions, with a TON of 5400. Furthermore, The catalytic consequences of Cl^- promotion in cyclopentane (CP) ring-opening on Pt/Al_2O_3 were demonstrated by Shi *et al.* [29]. Specifically, residual Cl^- induced the formation of electron-deficient Pt, which catalyzed the ring-opening of CP more efficiently than relatively neutral Pt atoms.

5. Influence mechanism of residual ions on catalysts

Residual ions can alter the structure and electronic environment of the active sites, affect the adsorption-desorption processes, and even interact with reaction products, thereby altering the overall catalytic performance. The effects of residual ions are complex, with the potential to both enhance and inhibit various stages of the catalytic process. Therefore, exploration of the multiple mechanisms of residual ions on catalysts and comprehension of their

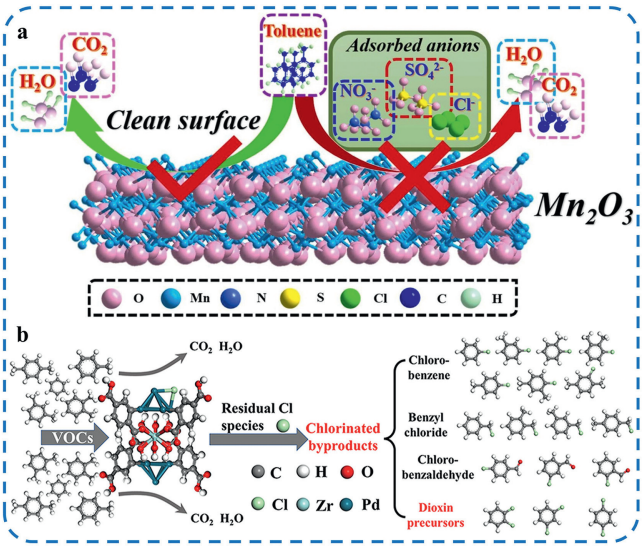


Fig. 4. (a) Mechanisms of the impact of residual anions on photothermal catalytic toluene degradation over Mn_2O_3. Copied with permission [46]. Copyright 2022, Elsevier. (b) Schematic illustration of the role of residual Cl^- in VOCs catalytic degradation and chlorinated byproduct formation. Copied with permission [25]. Copyright 2024, American Chemical Society.

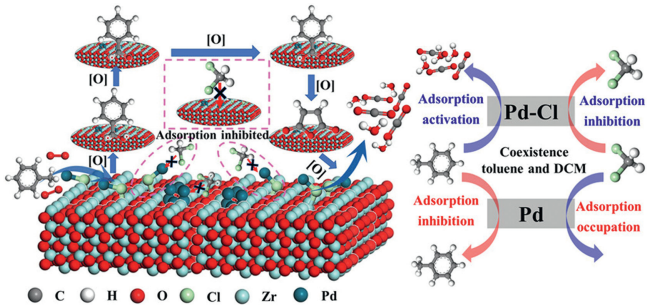


Fig. 5. Mechanism of residual chlorine-coordinated Pd single atoms in enhancing the chlorine resistance of Pd@ZrO_2 catalysts for the degradation of VOCs. Copied with permission [26]. Copyright 2022, American Chemical Society.

dual role in catalytic reactions are critical to optimize catalytic performance.

5.1. Inhibitory effect

In most cases, residual ions are a highly effective poison in the generation of the active site, either in terms of their number or their properties. As discussed in Section 3.1.1, residual Cl^- has been shown to coordinate and form complexes with metal centers and cause the aggregation of active metals in the catalyst particularly during the calcination process, thereby distorting the electronic structure of the metal centers and resulting in a reduced number of active sites. One representative example was that residual Cl^- could promote the agglomeration of Au particles during heat treatment through the formation of Au-Cl-Au bridges [33]. Some researchers have suggested that Au became active toward CO oxidation when its size was below 5 nm, which indicated the critical role of metal size in the catalysis process [104]. Moreover, for gold on CeO_2 support, Cl^- might combine with OVs in CeO_2 under reductive atmospheres to form CeOCl species. This combination stabilized the Ce^{3+} ions and reduced the oxygen storage capacity, which could affect the metal-support interaction and catalytic performance of the catalyst. Similarly, certain residual ions covered the surface of metal oxides or embedded into the lattice, which could inhibit the formation of OVs and block metal or active oxygen sites.

Catalytic reactions typically contain the steps of chemical adsorption of substrates, surface reaction, and product desorption [104]. These processes fundamentally rely on coordination or covalent interaction between active sites of catalysts and adsorbates, which could be significantly changed due to the presence of residual ions. For example, the anions of SO_4^{2-}, Cl^-, and NO_3^- on the surface of Mn_2O_3 inhibited the formation of $\cdot O^{2-}$ and $\cdot OH$ species, which were critical for the oxidation of intermediates such as benzyl alcohol and benzaldehyde. Therefore, these residual anions restrained the intermediate oxidation and cut off the reaction process of toluene oxidation (Fig. 4a). During the CO_2 hydrogenation on Ru/TiO_2 catalysts, the SO_4^{2-} at Ru/TiO_2 interface caused a significant enhancement of the hydrogen transfer process, as evidenced by detailed characterizations and density functional theory (DFT) calculations. The presence of SO_4^{2-} led to more H and electrons migrating from Ru to TiO_2 *via* the S medium, resulting in a reduction of H atoms on the Ru sites. The further hydrogenation of CO intermediates to CH_4 on Ru particles was inhibited. Consequently, this could effectively result in low product selectivity to CH_4.

Additionally, previous studies conducted by our research group have shown that residual Cl^- from the $ZrCl_4$ metal precursor was involved in the VOC degradation reaction, causing the formation of various chlorine-containing byproducts, even the hypertoxicity dioxin precursor, dichlorobenzene (Fig. 4b). The formation of these Cl-containing byproducts might result from the substitution reactions involving residual Cl species with methyl groups and H on benzene rings or methyl groups. Consequently, residual ions affect both the catalyst structure and active sites, while also reacting with contaminant substrates to generate more toxic pollutants, which further highlights the complex mechanisms of residual ions throughout the catalytic process.

5.2. Promoting effect

In some cases, residual ions can also play a promotive role in catalysis by enhancing the reactivity of catalysts or facilitating specific reaction pathways. Their promoting effects often depend on controlled concentrations and synergistic interactions with the catalyst components.

Residual Cl^-, for instance, has been shown to enhance Lewis acidity in metal catalysts, improving their activity in specific reactions. During the isomerization of allyl esters on Pt/CeO_2 catalysts containing residual Cl^-, the active species in this reaction are identified as highly dispersed Pt clusters composed of Pt-Cl and Pt-O bonds ($Pt(OH)_xCl_y$ and PtO_xCl_y) [30]. The Pt-Cl bonds lower the activation energy barrier and adsorption-desorption energy for the isomerization reaction, thus promoting the catalytic activity. Moreover, Cl^- acted to stabilize and enhance the acidity of the Pt centers, which was essential for the soft Lewis acid catalysis. Similarly, for the Pt/Al_2O_3 catalysts prepared from the Cl-containing precursor, Cl^- was observed to reduce the electron density of Pt and lower the intrinsic activation barrier for the C–C bond cleavage, which was rate-determining in the ring-opening reaction. It was demonstrated that electron-deficient Pt induced by Cl^- catalyzed the ring-opening of CP more efficiently than relatively neutral Pt atoms [29]. Our research group studied the role of residual chlorine-coordinated Pd single atoms in enhancing the chlorine resistance of Pd@ZrO_2 catalysts for the degradation of VOCs [26]. As shown in Fig. 5, the monodispersed Pd atoms and the generation of abundant OVs in the catalyst enhanced the adsorption and activation of gaseous oxygen molecules. The presence of Pd_1-Cl species suppressed the adsorption of DCM, thereby releasing more active sites for the adsorption of toluene and its intermediates. The

formation of Pd_1-Cl species was the critical factor to improve the chlorine resistance.

Furthermore, residual ions improve the dispersion of active metals or enhance the textural properties of the support. For example, residual SO_4^{2-} on NiMo/γ-Al_2O_3 catalysts promoted the sulfidation of *M. species*, increasing the formation of Ni-Mo-S active sites and boosting hydrodesulfurization activity [52]. Similarly, residual Na^+ could stabilize certain crystalline phases, such as in Al-rich zeolites, where optimal Na^+ content enhanced framework stability and high-temperature performance [63]. Residual ions could also accelerate reaction mechanisms by improving charge transfer or stabilizing intermediates. In the OER, SO_4^{2-} enhanced catalytic activity by stabilizing OOH* intermediates and accelerating charge transfer. This effect was particularly evident in NiFe (oxy)hydroxide catalysts, where SO_4^{2-} reduced charge transfer resistance, achieving higher activity [48].

In summary, residual ions can significantly enhance catalytic performance in some cases through the promotion of active metal dispersion, stabilization of catalytic intermediates, and enhancement of charge transfer. The beneficial effects are highly dependent on their specific interactions with the catalyst and reaction conditions, highlighting the importance of careful control over their presence and concentration in catalyst design.

6. Conclusion and prospect

This paper systematically reviews the impact of residual ions on the structure and performance of catalysts, with a particular focus on ions introduced during the catalyst preparation. Although the presence of residual ions is often overlooked, they play a crucial role in catalytic reactions, exerting both positive and negative effects. These ions can interact with the active sites and supports of catalysts, which lead to alterations in their electronic structure, geometric structure, and chemical properties. In addition to structural modifications, residual ions can also influence the adsorption and desorption processes of reactants and products on the catalyst surface, which can further affect catalytic activity and selectivity in a range of reactions, such as oxidation, hydrogenation, and others. An understanding of the intricate relationship between these ions and catalytic performance is crucial for the design of more efficient and durable catalysts.

To further explore the potential value of the relationship between residual ions and catalytic performance and advance the development of the catalyst field, the focus of future research is as follows.

(1) By utilizing more advanced in situ characterization techniques to observe the behavior of residual ions during the catalyst preparation and reaction processes in real time, the depth of fundamental research can be promoted. Combined with multiscale simulation methods, precise theoretical models can be constructed to predict the effects of various residual ions in different catalytic systems, providing theoretical guidance for experimental studies.

(2) Future research should focus on improving preparation techniques to achieve precise control over the type, content, and distribution of residual ions. Methods such as atomic layer deposition (ALD) and microfluidic technology can be employed to enhance the uniformity and stability of catalysts. For instance, new synthesis methods like ALD facilitate the precise control of residual ions. The use of efficient impurity removal technologies, such as ion-exchange resins, offers the potential to remove harmful ions without compromising catalytic performance.

(3) Based on the understanding of the impact of residual ions, the design of novel, highly efficient catalysts should be pursued. For example, the introduction of specific residual ions could be used to regulate the electronic properties of active sites, thereby enabling efficient catalysis of complex reactions. Furthermore, the research findings will extend into emerging catalytic fields, offering potential solutions for energy and environmental challenges.

(4) Under real operating conditions such as high temperature, high pressure, and complex reaction atmosphere, residual ions may induce structural changes or poisoning in catalysts. Therefore, it is essential to investigate the specific effects of residual ions on catalytic performance under different conditions, providing crucial insights for the optimization of catalytic processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yaofei Zhang: Data curation, Formal analysis, Writing – original draft. **Jiani Chen:** Investigation, Formal analysis, Data curation. **Haotian Hu:** Investigation, Data curation. **Jianghua Huang:** Methodology, Software. **Jiafeng Wei:** Software, Methodology. **Fukun Bi:** Visualization, Supervision, Funding acquisition. **Xiaodong Zhang:** Supervision, Project administration, Writing – review & editing, Funding acquisition.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2025.111549.

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