

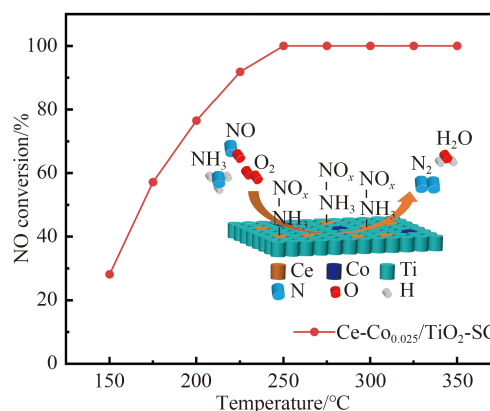
Study on the effect of preparation method on denitration performance of Co-modified Ce/TiO₂ catalyst

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Abstract: This study systematically conducted preparation optimization and performance investigations on Co-modified Ce/TiO₂ catalysts, with a focus on examining how preparation methods and Co loading regulate the catalyst's low-temperature denitrification activity. After identifying optimal preparation parameters *via* condition screening, multiple characterization techniques—including BET, XRD, XPS, H₂-TPR and *in situ* DRIFTS—were employed to deeply analyze the catalyst's physicochemical properties and reaction mechanism. Results demonstrated that compared to the impregnation and co-precipitation methods, the Ce-Co_{0.025}/TiO₂-SG catalyst (prepared by the sol-gel method with a Co/Ti mass ratio of 0.025) exhibited significantly superior denitrification activity: NO conversion remained stably above 95% in the 225–350 °C temperature range, and it displayed high N₂ selectivity. Characterization analysis revealed that abundant surface oxygen vacancies, a high proportion of Ce³⁺ species, and prominent acidic sites collectively contributed to enhancing its low-temperature denitrification performance. This work provides reference value for the development of highly efficient low-temperature denitrification catalysts.

Key words: preparation method; Co; Ce/TiO₂; low-temperature denitration; NH₃-SCR



Cement is widely used in fields such as transportation infrastructure, building structures, waterproofing projects, and renovation. Data from the National Bureau of Statistics shows that China's national cement output exceeded 2 billion tons in 2023, accounting for over 50% of the global total, and has remained the world's top producer for 38 consecutive years^[1]. However, the rapid development of the industry has also given rise to severe environmental problems. According to the 2020 China Ecological and Environmental Statistical Yearbook, cement manufacturing emitted 722000 t of nitrogen oxides (NO_x), accounting for 17.3% of total industrial source emissions. Effective control of NO_x has become an inevitable requirement for both ecological and environmental protection and the nation's sustainable economic development—making it urgent to accelerate the research, development, and promotion of denitrification technologies tailored to the cement industry.

Cement industry NO_x emission reduction technologies are primarily divided into two categories: process emission

reduction (combustion optimization) and end-of-pipe treatment, which differ significantly in denitrification efficiency and applicability. Process emission reduction achieves NO_x control by suppressing its formation, including low-nitrogen burners and staged combustion. Low-nitrogen burners inhibit thermal NO_x by optimizing coal-air mixing, reducing the excess air coefficient, and lowering flame temperature, though their efficiency is limited to 25%–35%. Staged combustion (fuel/air staging) reduces emissions *via* reactions in the reduction zone, yet its efficiency still falls below 40%, making both methods inadequate for ultra-low emission requirements. End-of-pipe treatment mainly uses selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR), which improve efficiency: SNCR achieves ~60% efficiency *via* high-temperature reactions without catalysts but suffers from high ammonia slip due to poor control over mixing and reaction conditions. SCR, leveraging catalysts, boosts efficiency to over 90% and minimizes ammonia slip by

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optimizing catalyst beds, temperature, and reductant injection, complying with ultra-low emission standards. Thus, SCR from end-of-pipe treatment is now one of the most reliable methods^[2].

In the field of denitrification catalysts, the development of high-efficiency, low-cost catalytic nanomaterials is the most critical link. Currently, cerium-based catalysts have emerged as a major research hotspot due to their unique advantages. As an environmentally friendly rare earth element, cerium (Ce) boasts low toxicity and high natural abundance—properties that align perfectly with the development trends of green chemistry.

With its distinct redox cycling capability and strong cost-effectiveness, Ce-based catalysts demonstrate significant application value in denitrification. The reversible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple endows the catalyst with efficient oxygen storage and release capacity^[3], promoting the conversion of NO to NO_2 and activating the “fast SCR reaction” pathway—both of which substantially enhance the catalyst’s low-temperature activity. Meanwhile, the surface of CeO_2 readily forms oxygen vacancies, which improve reactant adsorption and activation, further boosting low-temperature denitrification performance^[4]. Notably, unsupported Ce-based catalysts have drawbacks such as insufficient low-temperature activity. However, their performance can be effectively improved by dispersing them on a support material (i.e., loading onto a support).

Significant advances have been made in the modification of Ce-based catalysts. Sun et al.^[5] constructed a CeO_2 - TiO_2 gradient doping system. Experiments revealed that when the CeO_2 doping content reached 50%, the catalyst exhibited an amorphous structure—its high specific surface area and elevated oxygen vacancy concentration significantly enhanced the adsorption and activation efficiency of reactant molecules on the catalyst surface. Gao et al.^[6] investigated the performance of Ce-Ti mixed oxide catalysts with varying Ce loadings prepared *via* the sol-gel method and found that the catalyst with a 0.6 Ce loading displayed optimal catalytic activity.

Furthermore, compositing Ce with transition metals (e.g., Mn, Fe, Cu) can enhance low-temperature denitrification performance through synergistic effects: in the three-dimensionally ordered macroporous (3DOM) Ce-Fe composite catalyst developed by Liu et al.^[7], Fe doping markedly improved the catalyst’s reduction capacity, oxygen vacancy concentration, and amount of active oxygen species, while increasing its specific surface area and pore volume—providing more active sites.

In flue gas denitrification catalytic systems, although cobalt (Co) often acts as an active promoter rather than a primary catalyst, it significantly boosts denitrification efficiency *via* synergistic interactions. Its core role lies in forming electronic interactions with primary active components, optimizing the electron cloud density of surface active sites, and strengthening NH_3 adsorption/activation. Low-valent cobalt (Co^{3+}) donates electrons to promote NH_3 dissociation into more reactive

amino groups (NH_2), while high-valent cobalt (Co^{4+}) enhances NO oxidative adsorption through synergy with oxygen vacancies. This enables more efficient reduction reactions between NO and NH_3 on the catalyst surface, inhibiting the formation of by-product N_2O . Meanwhile, as a promoter, Co improves the distribution of acidic sites on the catalyst surface, adjusts the acidic strength of the support, and increases the proportion of weakly acidic sites—creating an acidic environment more conducive to selective NH_3 adsorption^[8–9].

Catalyst preparation methods directly influence their physicochemical properties, thereby dictating denitrification activity. Traditional Ce-based catalysts are mostly prepared *via* blending, whereas this study successfully synthesized a series of Ce-Co/ TiO_2 catalysts with different Co loadings using impregnation, sol-gel, and coprecipitation methods. We systematically investigated the impact of preparation methods on denitrification activity and combined characterization techniques (XRD, BET, SEM, H_2 -TPR, NH_3 -TPD, *in situ* DRIFTS) to conduct a comprehensive analysis of the catalysts’ physicochemical properties.

1 Experimental

1.1 Catalyst preparation

1.1.1 Impregnation method (IM)

Anatase nano- TiO_2 (Aladdin, 99.8%) was used as the catalyst support, and the catalyst was prepared *via* equivalent volume impregnation. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) served as metal precursors, dissolved in deionized water to prepare the impregnation solution based on the designed mass ratio. The impregnation solution was uniformly mixed with the TiO_2 support, then stirred in a water bath at 80 °C for 4 h to achieve uniform loading. Subsequently, it was dried in an oven at 110 °C for 12 h to remove moisture. Finally, the mixture was calcined in a muffle furnace with a heating rate of 5 °C/min to 500 °C and held for 3 h. The obtained catalyst was denoted as Ce-Co_x/ TiO_2 -IM, where *x* represents the Co/Ti mass ratio (*x* = 0.025, 0.05, 0.1).

1.1.2 Sol-gel method (SG)

The catalyst was prepared *via* the sol-gel method. A certain amount of deionized water was added to absolute ethanol. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) served as Ce and Co sources, respectively. The active components were dissolved in the mixed solution in stoichiometric proportions, followed by magnetic stirring for 1 h until fully dissolved (labeled as Solution A). Tetra-*n*-butyl titanate was used as the Ti source; anhydrous acetic acid was added dropwise to tetra-*n*-butyl titanate as a chelating agent, and

the mixture was stirred for 1 h (labeled as Solution B). Then, 0.75 mL of HNO_3 was added dropwise to Solution A to adjust the pH value to 1.0–2.0. Solution B was slowly dripped into Solution A with vigorous stirring for 2 h to form a transparent sol. After aging at room temperature in a fume hood for 48 h, the sol transformed into a gel. The gel was dried in an oven at 110 °C to remove organic solvents, then calcined in a muffle furnace at a heating rate of 5 °C/min to 500 °C for 3 h. The obtained catalyst was denoted as $\text{Ce-Co}_x/\text{TiO}_2\text{-SG}$, where x represents the Co/Ti mass ratio ($x = 0.025, 0.05, 0.1$).

For comparison, a Ce/TiO_2 catalyst was prepared *via* the same sol-gel method but without adding the Co source. It was denoted as $\text{Ce}/\text{TiO}_2\text{-SG}$.

1.1.3 Co-precipitation method (CP)

The catalyst was prepared *via* the co-precipitation method. Titanium oxysulfate was used as the Ti source; cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) served as Ce and Co sources, respectively. The active components were dissolved in deionized water in stoichiometric proportions and stirred for 4 h. Ammonia solution (3 mol/L) was added dropwise under stirring until the pH value reached ~10, inducing co-precipitation of metal hydroxides. The precipitate was aged at room temperature for 2 h and washed until pH value 7. The dried precipitate was calcined in a muffle furnace at a heating rate of 5 °C/min to 500 °C for 3 h (after drying at 110 °C for 12 h). The obtained catalyst was denoted as $\text{Ce-Co}_x/\text{TiO}_2\text{-CP}$, where x represents the Co/Ti mass ratio ($x = 0.025, 0.05, 0.1$).

1.2 Material characterization methods

The specific surface area and pore structure characteristics of the catalyst were determined using a fully automatic specific surface area and pore analyzer (ASAP 2020 Plus 2.00). The crystal structure of the catalyst was characterized by an X-ray diffractometer (XRD, Bruker D8). Cu- $K\alpha$ radiation source was used with a tube voltage of 30 kV, a scanning range of 10° to 80°, and a scanning speed of 10(°)/min. The valence state characteristics of surface elements were analyzed by X-ray photoelectron spectroscopy (Thermo Scientific k-alpha, USA) using an Al $K\alpha$ micro-focused monochromatic source as the X-ray excitation source. The redox properties of the sample were evaluated *via* temperature-programmed reduction ($\text{H}_2\text{-TPR}$) using a BSD-Chem C200 chemical adsorption analyzer. The surface acidity of the sample was obtained by temperature-programmed desorption ($\text{NH}_3\text{-TPD}$) with the same BSD-Chem C200 system. The surface adsorption behavior of the catalyst was studied using a Fourier transform infrared spectrometer (Nicolet 6700). All spectra were acquired with 32 accumulated scans over a range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} .

1.3 Catalyst performance testing

NO conversion was used as the core evaluation index for catalyst activity in this study. The simulated flue gas composition was 1.0×10^{-3} NO , 1.0×10^{-3} NH_3 , 5% O_2 , balanced with high-purity N_2 . The test temperature range was 150–350 °C. Prior to activity testing, the prepared catalysts were ground and sieved, and samples with a particle size of 40–60 mesh were selected. 0.2 mL of catalyst was placed in a quartz tube reactor with an inner diameter of 8 mm, and gas with a total flow rate of 200 mL/min (space velocity: 60000 h^{-1}) was introduced. The catalyst sample was fixed in the middle of the reactor with quartz wool to ensure uniform gas flow. A three-stage temperature-controlled tubular furnace was used to maintain the temperature required for the $\text{NH}_3\text{-SCR}$ reaction, ensuring uniform temperature distribution in the reactor. Meanwhile, a temperature-programmed test was conducted with a heating rate of 5 °C/min, using 25 °C as a data collection point. After heating by 25 °C and stabilizing for 10 min, the specific concentration of NO_x was recorded. A flue gas analyzer (Testo 350) was placed at the reactor outlet to measure NO_x concentration in real time.

2 Results and discussion

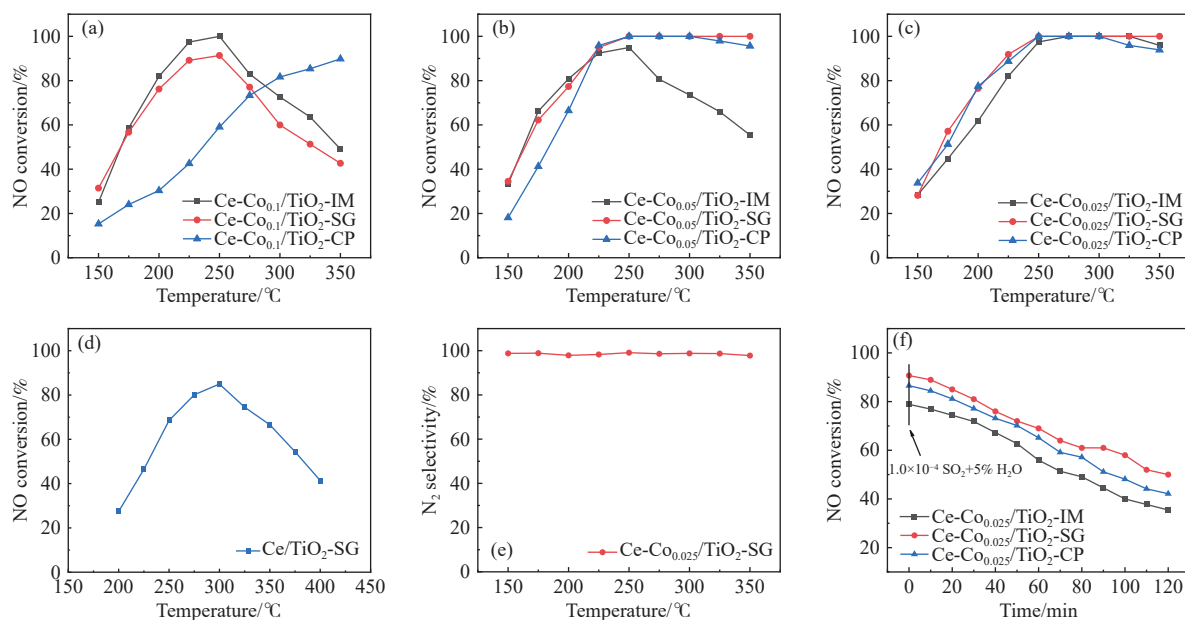
2.1 Catalyst activity evaluation

To systematically investigate the effects of preparation methods and Co/Ce mass ratio on the denitrification catalytic performance of the catalyst, TiO_2 was used as the support. Based on the mass of the Ti element, the mass fraction of Ce was fixed at 0.2, and the mass fractions of Co were adjusted to 0.025, 0.05 and 0.1, respectively. A series of catalysts were prepared and denoted as $\text{Ce-Co}_x/\text{TiO}_2$ ($x = 0.025, 0.05, 0.1$). The experiment used three typical methods—impregnation, sol-gel, and co-precipitation—to prepare samples separately. For each preparation method, the differences in denitrification activity of the catalyst under different Co/Ce mass ratios were focused on.

Activity test results (Figure 1(a)) show that in the temperature range of 150–250 °C, the NO conversion of the three catalysts increased gradually with rising temperature: the NO conversion of $\text{Ce-Co}_{0.1}/\text{TiO}_2\text{-IM}$ and $\text{Ce-Co}_{0.1}/\text{TiO}_2\text{-SG}$ increased from approximately 30% to around 90%. However, after exceeding 250 °C, their conversion decreased gradually with further temperature increase, presumably due to NH_3 being partially oxidized to NO as a reductant at high temperatures, leading to a decrease in reductant concentration and attenuation of denitrification efficiency. In contrast, $\text{Ce-Co}_{0.1}/\text{TiO}_2\text{-CP}$ showed a continuous upward trend throughout the test range. Further investigation of the effect of Co loading revealed that when the Co content was 0.05 (Figure 1(b)), $\text{Ce-Co}_{0.05}/\text{TiO}_2\text{-SG}$ and $\text{Ce-Co}_{0.05}/\text{TiO}_2\text{-CP}$ exhibited excellent activity, reaching approximately 90% NO removal at 225 °C. $\text{Ce-Co}_{0.05}/\text{TiO}_2\text{-$

CP and Ce-Co_{0.1}/TiO₂-SG had similar activity trends. When the Co content decreased to 0.025 (Figure 1(c)), the activities of the three catalysts converged, all achieving nearly complete NO removal at 250 °C. Compared to other types of cerium-based catalysts, the catalysts in this study still exhibit relatively obvious advantages in denitrification performance (as shown in Table 1). Compared to the Co-free Ce/TiO₂-SG catalyst (Figure 1(d)), which only reached approximately 80% conversion at 300 °C, the introduction of Co not only significantly enhanced the NH₃-SCR activity in the medium and low temperature regions but also effectively broadened the temperature window.

Regarding nitrogen selectivity, a key indicator of NH₃-SCR technology, Ce-Co_{0.025}/TiO₂-SG maintained N₂ selectivity above 95% across the entire temperature range (150–350 °C) (Figure 1(e)). However, small amounts of H₂O and SO₂ present in actual flue gas have a significant adverse effect on catalyst performance: tests in Figure 1(f) show that after adding 1.0×10⁻⁴ SO₂ and 5% H₂O to the simulated flue gas at 220 °C, the NO_x conversion efficiency of all three catalysts decreased. After 2 h of reaction, the NH₃-SCR efficiency dropped below 50%, indicating that these catalysts have not yet demonstrated excellent sulfur and water resistance stability.



(a): Ce-Co_{0.1}/TiO₂; (b): Ce-Co_{0.05}/TiO₂; (c): Ce-Co_{0.025}/TiO₂; (d): NH₃-SCR of Ce/TiO₂-SG catalyst; (e): N₂ selectivity of Ce-Co_{0.025}/TiO₂-SG; (f): sulfur and water resistance of the three catalysts.

Fig. 1 NH₃-SCR of the Ce-Co_x/TiO₂ catalysts (x=0.025, 0.05, 0.1) prepared by different methods

Table 1 Performance comparison of cerium-based catalysts

Catalyst	Flue gas conditions and space velocity	$t_{100}/^{\circ}\text{C}$	Reference
CeO ₂ /TiO ₂	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 5% O ₂ , 120000 mL/(g h)	400	[10]
CeO _x S _{0.1}	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 5% O ₂ , 40000 h ⁻¹	275	[11]
15%FeV/CeO ₂ -S	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 5% O ₂ , 80000 mL/(g h)	250	[12]
CeO ₂ @ZSM-5	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 10% O ₂ , 45000 h ⁻¹	250	[13]
Ce _{0.95} W _{0.05} O ₂ -TA	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 5% O ₂ , 200000 mL/(g h)	350	[14]
Cu/(ZSM-5@CeO ₂)	1.0×10^{-3} NH ₃ , 1.0×10^{-3} NO, 8% O ₂ , 50000 h ⁻¹	250	[15]
Ti _{0.10} -CeO ₂	6.0×10^{-4} NH ₃ , 6.0×10^{-4} NO, 3% O ₂ , 72000 mL/(g h)	250	[16]
20CeO ₂ /Ti-Zr-S	6.0×10^{-4} NH ₃ , 6.0×10^{-4} NO, 5% O ₂ , 60000 h ⁻¹	250	[17]
CeO ₂ -WO ₃ -hexagonal	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 5% O ₂ , 30000 h ⁻¹	260	[18]
7Ce-VW/Ti	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 5% O ₂ , 160000 h ⁻¹	225	[19]
W/CeO ₂ -Rod	5.0×10^{-4} NO, 5.0×10^{-4} NH ₃ , 5% O ₂ , 90000 mL/(g h)	250	[20]
Ce-Co _{0.025} /TiO ₂ -SG	1.0×10^{-3} NO, 1.0×10^{-3} NH ₃ , 5% O ₂ , 45000 h ⁻¹	250	this study

2.2 BET analysis of catalysts

To systematically reveal the regulatory rules of synthesis methods on the mesoporous structure and surface properties of Ce-Co_{0.025}/TiO₂ catalysts, three target catalysts prepared by different methods were selected, and their mesoporous structures were characterized *via* N₂ adsorption-desorption experiments. The relevant pore structure parameters are listed in Table 2. The N₂ adsorption-desorption isotherms obtained from the experiments are presented in Figure 2 and the corresponding BJH pore size distribution curves are also shown in Figure 3.

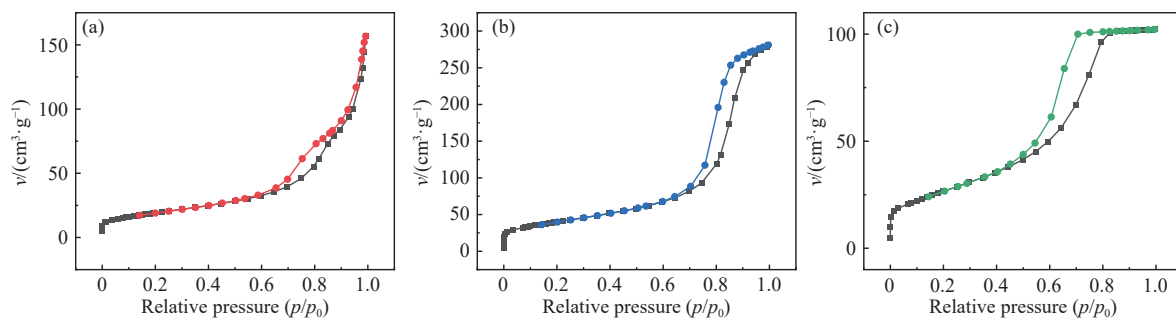
All catalysts exhibited typical type IV adsorption-desorption isotherms^[21]. Combined with the average pore size data in Table 2, this clearly confirms their mesoporous structural characteristics. Notably, significant differences were observed in the morphology and position of the hysteresis loops among catalysts prepared by different methods, reflecting subtle regulation of mesoporous structures: The Ce-Co_{0.025}/TiO₂-IM catalyst prepared by the impregnation method displayed an H4-type hysteresis loop, a typical feature of slit-like mesopores or mesopores with narrow size distributions^[22]. Based on analysis of its preparation process, active components were primarily loaded onto the carrier surface without significantly altering the original pore structure of the carrier. Thus, its mesopores were dominated by parallel plate-like slit pores, characterized by lower pore volume and concentrated pore size distribution. The Ce-Co_{0.025}/TiO₂-CP catalyst prepared by coprecipitation exhibited an H1-type hysteresis loop, which is generally associated with mesopores formed by particle stacking. It is inferred that during coprecipitation,

active components interacted with the carrier to form composite structures^[23]. Particle stacking during this process generated abundant mesopores with a relatively wide size distribution (still with some distribution in the 20–30 nm range), possibly related to macropores formed during stacking. The Ce-Co_{0.025}/TiO₂-SG catalyst prepared by the sol-gel method showed an H2-type hysteresis loop, closely linked to hierarchical pore structures formed during gelation. Its mesopores featured a wider size distribution and varying pore connectivity, resulting in more complex pore structures characterized by narrower size distribution and dominance of small mesopores.

Further comparison of the pore structure parameters (Table 2) revealed the following order: (1) Specific surface area: Ce-Co_{0.025}/TiO₂-CP > Ce-Co_{0.025}/TiO₂-SG > Ce-Co_{0.025}/TiO₂-IM; (2) Pore volume: Ce-Co_{0.025}/TiO₂-CP > Ce-Co_{0.025}/TiO₂-IM > Ce-Co_{0.025}/TiO₂-SG; (3) Average pore diameter: Ce-Co_{0.025}/TiO₂-IM > Ce-Co_{0.025}/TiO₂-CP > Ce-Co_{0.025}/TiO₂-SG. This trend was highly correlated with the hysteresis loop types and mesoporous structural characteristics. Differences in thermodynamic mechanisms, solvent environments, and post-treatment conditions among preparation methods all contributed to variations in pore structure and specific surface area. The pore structure characteristics of the three catalysts after reaction are listed in Table 2. Compared to fresh samples, there were no significant differences in physical properties such as pore structure, indicating minimal changes in physical properties before and after the reaction. In summary, physical factors such as pore structure and specific surface area are not the primary influences on NH₃-SCR performance.

Table 2 Textural properties of various catalysts

Catalyst	BET/(m ² ·g ⁻¹)	Pore volume/(cm ³ ·g ⁻¹)	Average pore size/nm
Ce-Co _{0.025} /TiO ₂ -IM	69.10	0.24	12.69
Ce-Co _{0.025} /TiO ₂ -CP	143.80	0.43	9.96
Ce-Co _{0.025} /TiO ₂ -SG	97.00	0.16	5.05
Ce-Co _{0.025} /TiO ₂ -IM-used	67.43	0.23	12.72
Ce-Co _{0.025} /TiO ₂ -CP-used	144.65	0.43	9.85
Ce-Co _{0.025} /TiO ₂ -IM-used	96.65	0.15	5.12



(a): Ce-Co_{0.025}/TiO₂-IM; (b): Ce-Co_{0.025}/TiO₂-CP; (c): Ce-Co_{0.025}/TiO₂-SG.

Fig. 2 N₂ adsorption-desorption isotherms for various catalysts

2.3 XRD analysis of catalysts

Figure 4 presents the X-ray diffraction (XRD) patterns of Ce-Co_{0.025}/TiO₂ catalysts prepared by different methods. It can be observed that all catalysts exhibit characteristic diffraction peaks of the anatase TiO₂ support (JCPDS 21-1272), with main diffraction peaks appearing at 25.42°, 38.00°, 47.98°, 54.12°, 55.46°, 62.88°, 70.08° and 76.42°, corresponding to the (101), (004), (200), (105), (211), (213), (116) and (215) crystal planes of anatase TiO₂, respectively^[24]. Further analysis revealed additional diffraction peaks at 28.82° (corresponding to the (111) plane) and 33.48° (corresponding to the (200) plane) in the pattern of Ce-Co_{0.025}/TiO₂-IM, which were attributed to fluorite-structured CeO₂ (JCPDS 34-0394)^[25], indicating high crystallinity and microcrystalline existence of CeO₂ in this catalyst. Notably, no characteristic diffraction peaks of Co species were detected in any sample, suggesting that Co components might be highly dispersed or present in an amorphous state on the carrier surface. This result is consistent with the findings of Gao et al.^[26] and Yao et al.^[27].

Additionally, both anatase TiO₂ and CeO₂ phases were observed in Ce-Co_{0.025}/TiO₂-IM. The TiO₂ diffraction peaks were intense and sharp, confirming that TiO₂ existed predominantly in the anatase phase with excellent crystallinity. Although the CeO₂ peaks (e.g., at 28.82°) were weaker than those of TiO₂, they were still clearly present, indicating a small amount of CeO₂ crystallites dispersed in the catalyst.

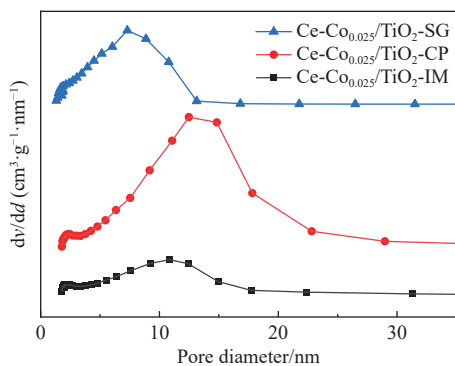


Fig. 3 Pore size distributions for various catalysts

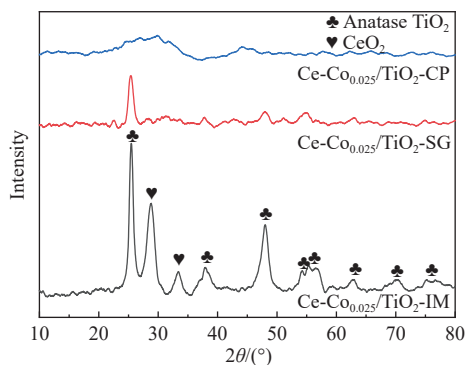


Fig. 4 XRD patterns of various catalysts

Ce-Co_{0.025}/TiO₂-SG also exhibited characteristic peaks of anatase TiO₂ and CeO₂, but with fewer peaks and significantly weaker intensities compared to Ce-Co_{0.025}/TiO₂-IM. The main TiO₂ peaks were obviously broadened and weakened, while the CeO₂ peaks became blurred, suggesting reduced crystallinity of both phases. This may be due to the inhibition of grain growth or the formation of a large amount of amorphous phase encapsulating grains during the precursor hydrolysis/condensation process in sol-gel synthesis, thereby lowering crystallinity.

In contrast, Ce-Co_{0.025}/TiO₂-CP showed almost no distinct characteristic diffraction peaks, with no obvious anatase TiO₂ or CeO₂ crystalline phase peaks observed. This indicates that the sample was predominantly amorphous or composed of extremely small grains, possibly because the grains failed to effectively crystallize during the precipitation process. In summary, the three samples exhibited significant differences in crystal structure (phase composition, crystallinity, and grain size) due to their distinct preparation processes^[28–29], which may be one of the reasons for the variations in their NH₃-SCR performance.

2.4 XPS analysis of catalysts

To deeply investigate the chemical states of surface elements on the catalysts, XPS measurements were performed to obtain the characteristic spectra of the O 1s and Ce 3d orbitals (Figures 5(a)–(f)). The surface atomic percentage compositions of each catalyst were then calculated based on peak areas (Table 2).

Analysis of the O 1s spectra revealed significant differences in surface oxygen species among the three catalysts: Both Ce-Co_{0.025}/TiO₂-IM and Ce-Co_{0.025}/TiO₂-CP exhibited two main peaks in their O 1s spectra. The peaks at binding energies of 530.0–531.0 eV corresponded to lattice oxygen (O_β, oxygen species bound to the TiO₂ lattice), while those at 531.0–532.0 eV were attributed to adsorbed oxygen (O_α, oxygen species physically or weakly chemically adsorbed on the surface)^[30]. Notably, the O 1s spectrum of Ce-Co_{0.025}/TiO₂-SG displayed an additional third peak (approximately 532.5–533.5 eV), assigned to surface oxygen-containing functional groups (O_γ), which were speculated to originate from surface hydroxyl groups (–OH) or carbonate groups (CO₃^{2–}) formed during the hydrolysis and condensation of tetrabutyl titanate in the sol-gel process^[31]. Importantly, O_γ was only detected in the SG sample, a feature closely linked to differences in the preparation process. Previous studies have shown that O_α is the most active oxygen species in oxidation reactions, with significantly better migration ability than O_β. Abundant O_α not only promotes the oxidation of NO to NO₂ (increasing the concentration of key intermediates in the SCR reaction) but also fills oxygen vacancies and accelerates the Ce⁴⁺/Ce³⁺ redox cycle^[32]. Combining the data in Table 3, Ce-Co_{0.025}/TiO₂-IM had the lowest O_α content (insufficient exposure of active sites), leading to relatively weaker catalytic activity, which aligns with the activity test results.

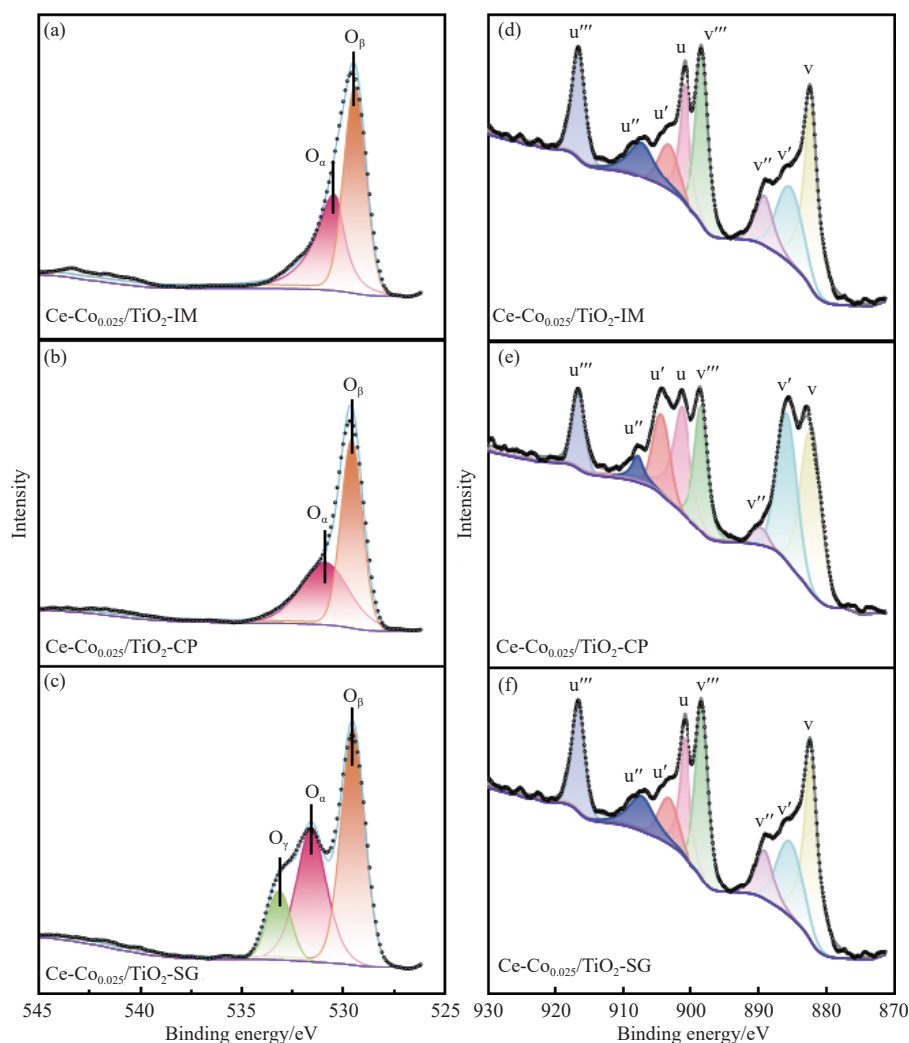


Fig. 5 XPS spectra for O 1s (a)–(c) and Ce 3d (d)–(f) of various catalysts

Table 3 Surface atomic content ratios of the catalysts

Catalyst	O_a/O_a+O_β (atom%)	Ce^{3+}/Ce^{4+} (atom%)
Ce- $Co_{0.025}/TiO_2$ -IM	11.24	27.49
Ce- $Co_{0.025}/TiO_2$ -CP	60.23	47.60
Ce- $Co_{0.025}/TiO_2$ -SG	39.63	44.68

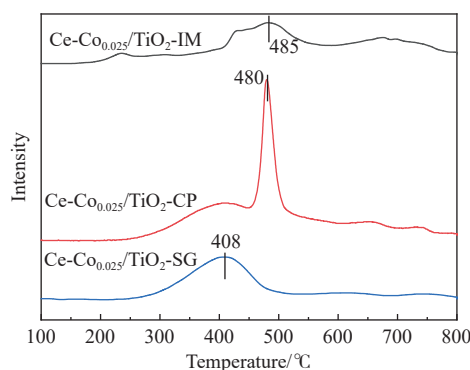
In contrast, the SG and CP samples exhibited higher O_a content, potentially providing a basis for their superior SCR performance through oxygen species availability.

As shown in Figures 5(d)–(f), the Ce 3d XPS spectra displayed eight coexisting peaks, labeled as μ''' (917.0 eV), μ'' (907.8 eV), μ' (904.7 eV), μ (902.2 eV), v''' (899.3 eV), v'' (886.7 eV), v' (885.3 eV) and v (882.7 eV). Among these, the characteristic peaks at μ' and v' corresponded to Ce^{3+} , while the remaining six peaks were attributed to Ce^{4+} [33]. Ce in CeO_2 exhibits unique redox properties, with changes in oxidation state *via* $Ce^{3+} \leftrightarrow Ce^{4+}$, demonstrating excellent oxygen storage and release capacity. Ce^{3+} originates from lattice defects in Ce, inducing electron transfer due to charge imbalance, which increases surface O_a and unsaturated chemical bonds, thereby promoting the $Ce^{3+} \leftrightarrow Ce^{4+}$ redox cycle[34]. It can be observed that Ce^{4+} was the

dominant form of Ce in the catalysts, with the Ce^{3+}/Ce^{4+} ratio positively correlated to oxygen vacancy concentration[35]. Both coprecipitation and sol-gel methods retained a significant amount of Ce^{3+} , markedly enhancing the redox properties of the catalysts. In contrast, the Ce- $Co_{0.025}/TiO_2$ -IM catalyst had a lower Ce^{3+} proportion (27.49%). The preparation method of the catalyst influenced the composition and oxidation state of surface metal ions, and higher O_a and Ce^{3+} proportions may be among the reasons for the superior performance of the coprecipitation and sol-gel method catalysts.

2.5 H₂-TPR analysis of catalysts

Figure 6 presents the H₂-temperature-programmed reduction (H₂-TPR) profiles of catalysts prepared by different methods. The temperature of reduction peaks in the H₂-TPR profiles directly reflects the ease of reduction of active components (e.g., metal oxides) in the catalyst—lower reduction peak temperatures indicate stronger reducibility of active components, weaker metal-support interactions, or higher dispersion of active components[36].

Fig. 6 H₂-TPR profiles of various catalysts

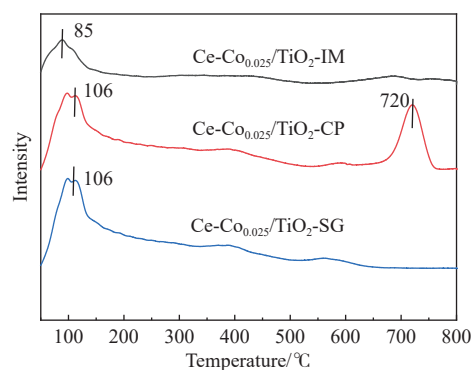
Specifically, the high-temperature reduction peaks at 450–550 °C correspond to the transformation process of CeO₂ to Ce₂O₃^[37]. Among them, the reduction peak temperatures of Ce-Co_{0.025}/TiO₂-IM and Ce-Co_{0.025}/TiO₂-CP were similar, while that of Ce-Co_{0.025}/TiO₂-SG was the lowest, indicating that the catalyst prepared by the sol-gel method had higher dispersion of active components, weaker metal-support interactions, and was more easily reduced by H₂^[38]. Notably, Ce-Co_{0.025}/TiO₂-CP exhibited the highest reduction peak intensity, suggesting the fastest reduction rate of its surface active sites. This may be related to the formation of highly dispersed active components (e.g., Co₃O₄-CeO₂ composite oxides) through the homogeneous precipitation process—such composite structures provide abundant surface oxygen vacancies and metal active centers, promoting the reduction reaction with H₂.

Combining the characteristics of reduction peak temperatures and intensities, Ce-Co_{0.025}/TiO₂-SG, with the lowest reduction peak temperature, exhibited better reduction performance in the low-to-medium temperature region. Ce-Co_{0.025}/TiO₂-CP, with the highest peak intensity, demonstrated a superior number of active sites and reduction kinetic properties. In contrast, Ce-Co_{0.025}/TiO₂-IM had the highest reduction peak temperature and smallest peak area, indicating poorer dispersion of active components. The strong interactions between Co-O-Ce bonds weakened the strength of Co-O-Co bonds^[39], increasing the difficulty of reduction. These differences stem from the regulation of synergistic effects among Ce, Co, and Ti species by different preparation methods.

2.6 NH₃-TPD analysis of catalysts

NH₃-temperature-programmed desorption (NH₃-TPD) tests were conducted to analyze the surface acid amount and acid strength characteristics of catalysts prepared by different methods, with results shown in Figure 7. During the temperature-programmed desorption process, NH₃ adsorbed on Lewis acid sites (L-acid) typically desorbs at lower temperatures than NH₃ coordinated to Brønsted acid sites (B-acid)^[40].

The NH₃-TPD profile of the Ce-Co_{0.025}/TiO₂-IM catalyst exhibited only a weak peak at 85 °C, corresponding to physically adsorbed NH₃ or NH₃ adsorbed on extremely weak B-acid sites.

Fig. 7 NH₃-TPD profiles of various catalysts

This characteristic indicates a scarcity of surface acidic sites, which may lead to insufficient low-temperature SCR activity^[41]. The spectrum of the Ce-Co_{0.025}/TiO₂-SG catalyst showed a moderate-strong peak at 106 °C, which was speculated to be related to the uniform mesoporous structure formed by the sol-gel method—this structure increased the exposed quantity of acidic sites, making it more suitable for low-to-medium temperature reaction requirements. Notably, the quantity of medium- and low-strength acidic centers on the catalyst surface directly affects the adsorption and activation of molecules within the denitration reaction temperature window, a key factor determining catalytic activity^[42].

The spectrum of the Ce-Co_{0.025}/TiO₂-CP catalyst also exhibited a moderate-strong peak at 106 °C, similar to that of the SG catalyst (corresponding to medium-strength acid sites)^[43–44]. The appearance of this high-temperature peak indicates that the coprecipitation preparation process increased the number of strong acid centers in the catalyst, which is not only beneficial for NH₃ adsorption but may also enhance the catalyst's high-temperature stability.

2.7 In situ DRIFTS analysis of catalysts

To investigate the NH₃-SCR reaction mechanisms of different catalysts, this study analyzed the reaction pathways on the surface of the Ce-Co_{0.025}/TiO₂-IM catalyst using NH₃ pre-adsorption and NO+O₂ pre-adsorption experiments combined with *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS). During the experiment, NH₃ pre-adsorption was first performed: NH₃ was introduced into the catalyst bed at 200 °C and pre-adsorbed for 60 min to saturation. Subsequently, N₂ was used to purge the catalyst for 20 min to remove physically adsorbed NH₃, after which a NO+O₂ mixture was introduced. As shown in Figure 8(a), after pre-adsorption, only weak NH₃ adsorption peaks on L-acid sites (1598 cm⁻¹)^[45] and L-acid site -NH₂ species peaks (1310 cm⁻¹)^[46] were observed on the catalyst surface. However, after introducing NO+O₂, the intensities of these NH₃-related peaks did not significantly decrease, and no new characteristic product peaks were observed. This phenomenon indicates that on the surface of Ce-

$\text{Co}_{0.025}/\text{TiO}_2\text{-IM}$, the pre-adsorbed NH_3 was not consumed by $\text{NO}+\text{O}_2$, and no direct $\text{NH}_3\text{-NO}$ catalytic reaction occurred.

Further $\text{NO}+\text{O}_2$ pre-adsorption experiments were conducted: Similarly, $\text{NO}+\text{O}_2$ was pre-adsorbed onto the catalyst surface at 200°C to saturation (60 min), and after purging with N_2 for 20 min, NH_3 was introduced. Figure 8(b) shows that after $\text{NO}+\text{O}_2$ pre-adsorption, characteristic absorption peaks appeared at $1600/1520\text{ cm}^{-1}$ (corresponding to NO_2 molecules^[47]) and $1312/1264\text{ cm}^{-1}$ (corresponding to monodentate nitrates)^[48]. After introducing NH_3 , the absorption peak intensities of nitrate species gradually decreased, while new L-acid site N-H species peaks ($3363, 3264, 3166\text{ cm}^{-1}$)^[49] and NH_3 species peaks (1189 cm^{-1})^[50] appeared. This change indicates that NH_3 needs to act synergistically with adsorbed NO_x (e.g., nitrates) rather than directly reacting with gaseous NO , which is consistent with the characteristics of the Langmuir-Hinshelwood (L-H) reaction mechanism. In summary, the $\text{NH}_3\text{-SCR}$ reaction on the surface of the $\text{Ce-Co}_{0.025}/\text{TiO}_2\text{-IM}$ catalyst preferentially follows the L-H mechanism, where adsorbed NH_3 and adsorbed NO_x synergistically react on surface active sites to generate products.

The results of the *in situ* DRIFTS analysis of the $\text{NH}_3\text{-SCR}$ reaction on the surface of the $\text{Ce-Co}_{0.025}/\text{TiO}_2\text{-CP}$ catalyst are shown in Figure 9, which examined the reaction

processes following NH_3 pre-adsorption with subsequent $\text{NO}+\text{O}_2$ introduction, and $\text{NO}+\text{O}_2$ pre-adsorption with subsequent NH_3 introduction.

For the NH_3 pre-adsorption experiment: After pre-adsorbing NH_3 to saturation at 200°C , characteristic NH_3 adsorption peaks on L-acid sites (1598 cm^{-1}) first appeared on the catalyst surface. Meanwhile, a symmetric bending vibration peak of the N-H bond in NH_3 was observed at 1315 cm^{-1} ^[51]. Upon introducing $\text{NO}+\text{O}_2$, the NH_3 adsorption peak at 1598 cm^{-1} rapidly diminished and was consumed, while the N-H bending vibration peak at 1315 cm^{-1} gradually disappeared within 10 min. Subsequently, a characteristic absorption peak of bridging nitrate species emerged at 1426 cm^{-1} ^[52]. This sequence of peak changes indicates that the pre-adsorbed NH_3 reacted chemically with NO , forming bridging nitrate intermediate species. The reaction process aligns with the characteristics of the Langmuir-Hinshelwood (L-H) mechanism—where adsorbed NH_3 and adsorbed NO_x synergistically react on surface active sites to generate products.

For the $\text{NO}+\text{O}_2$ pre-adsorption experiment: After pre-adsorbing $\text{NO}+\text{O}_2$ to saturation at 200°C , multiple characteristic peaks of nitrate species appeared on the catalyst surface, corresponding to NO_2 molecules (1600 cm^{-1}), bidentate nitrates (1565 cm^{-1}), monodentate nitrates (1314 cm^{-1}), and bridging nitrates (1240 cm^{-1}).

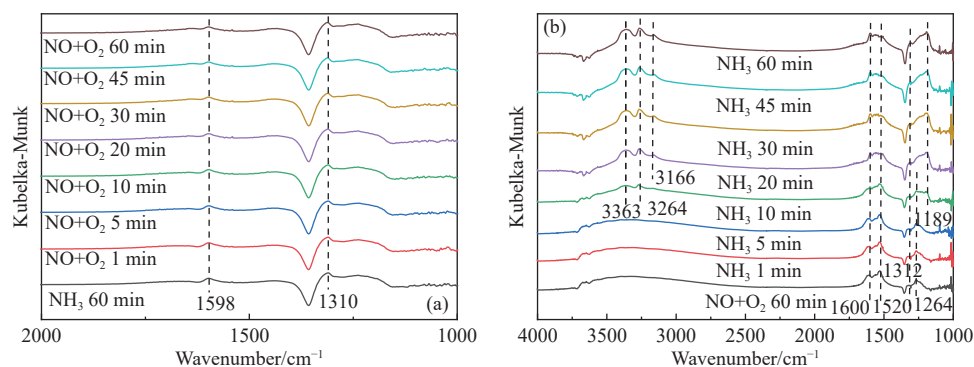


Fig. 8 *In situ* DRIFTS spectra of reaction at 200°C between $\text{NO} + \text{O}_2$ and pre-adsorbed NH_3 (a), NH_3 and pre-adsorbed $\text{NO} + \text{O}_2$ (b) on $\text{Ce-Co}_{0.025}/\text{TiO}_2\text{-IM}$

Reaction condition: 1.0×10^{-3} NO , 1.0×10^{-3} NH_3 , 5% O_2 , N_2 as equilibrium gas, space velocity of 60000 h^{-1} , 200°C .

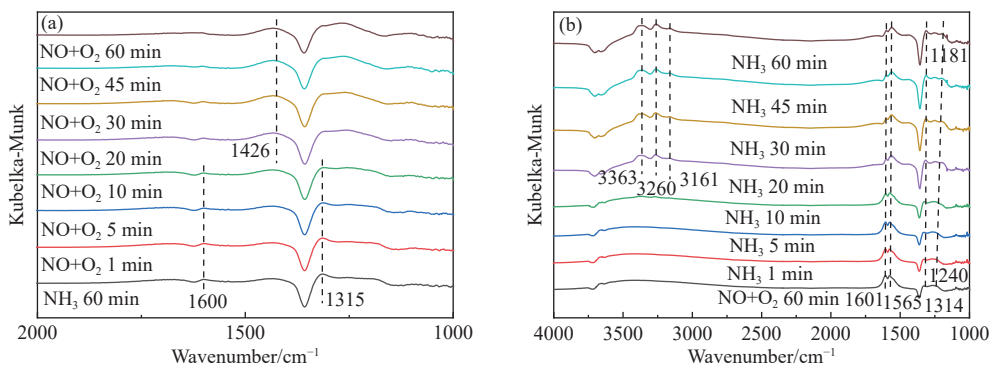


Fig. 9 *In situ* DRIFTS spectra of reaction at 200°C between $\text{NO} + \text{O}_2$ and pre-adsorbed NH_3 (a), NH_3 and pre-adsorbed $\text{NO} + \text{O}_2$ (b) on $\text{Ce-Co}_{0.025}/\text{TiO}_2\text{-CP}$

Reaction condition: 1.0×10^{-3} NO , 1.0×10^{-3} NH_3 , 5% O_2 , N_2 as equilibrium gas, space velocity of 60000 h^{-1} , 200°C .

Upon introducing NH_3 , the bridging nitrate peak at 1240 cm^{-1} gradually transformed into an NH_3 characteristic peak at 1181 cm^{-1} , suggesting that some nitrate species participated in the reaction with NH_3 . However, unlike the NH_3 pre-adsorption experiment, the nitrate peaks (e.g., at 1600 , 1565 and 1314 cm^{-1}) after $\text{NO}+\text{O}_2$ pre-adsorption did not decrease significantly, and they coexisted with the NH_3 peaks for a long time after NH_3 introduction. This phenomenon may be attributed to the limited reactivity of the L-H mechanism at the current reaction temperature, leading to a slower consumption rate of nitrate species and incomplete conversion to products. In summary, the NH_3 -SCR reaction on the surface of the $\text{Ce-Co}_{0.025}/\text{TiO}_2$ -CP catalyst exhibited L-H mechanism characteristics under both pre-adsorption conditions. Nevertheless, the residual nitrate species after $\text{NO}+\text{O}_2$ pre-adsorption suggest that its reaction kinetics may be influenced by temperature or active site distribution.

The results of the *in situ* DRIFTS analysis of the NH_3 -SCR reaction on the surface of the $\text{Ce-Co}_{0.025}/\text{TiO}_2$ -SG catalyst are shown in Figure 10, which examined the reaction processes following NH_3 pre-adsorption with subsequent $\text{NO}+\text{O}_2$ introduction, and $\text{NO}+\text{O}_2$ pre-adsorption with subsequent NH_3 introduction.

For the NH_3 pre-adsorption experiment: After pre-adsorbing NH_3 to saturation at $200\text{ }^\circ\text{C}$, multiple characteristic peaks appeared on the catalyst surface. These included characteristic peaks of NH_3 species on L-acid sites (1606 , 1197 cm^{-1}), absorption peaks of NH_4^+ species on B-acid sites (1420 cm^{-1}), and peaks of $-\text{NH}_2$ species adsorbed on L-acid sites (1322 cm^{-1}), indicating that NH_3 adsorbed on the surface in multiple forms. Upon introducing NO , the peak intensity at 1600 cm^{-1} gradually increased, which was

speculated to overlap with the absorption peak of NO_2 molecules. Notably, no characteristic peaks of nitrate species were observed throughout the experiment, suggesting that nitrate intermediates were not generated, and the reaction may have directly produced N_2 and H_2O . Furthermore, all adsorption-related peaks (e.g., those of NH_3 , NH_4^+ and $-\text{NH}_2$) gradually disappeared after 60 min, indicating that the pre-adsorbed NH_3 and converted NH_4^+ had participated in the reaction and been consumed by NO , consistent with the characteristic synergistic reaction of adsorbed species in the Langmuir-Hinshelwood (L-H) mechanism.

For the $\text{NO}+\text{O}_2$ pre-adsorption experiment: After pre-adsorbing $\text{NO}+\text{O}_2$ to saturation at $200\text{ }^\circ\text{C}$, only the characteristic absorption peak of NO_2 molecules at 1610 cm^{-1} was observed on the catalyst surface, consistent with the previously proposed formation of NO_2 . Upon introducing NH_3 , NH_3 -related characteristic peaks appeared on the surface, but no absorption peaks of nitrate species were detected. This phenomenon suggests that the reaction on the catalyst surface primarily occurred between gaseous NO_x (e.g., NO_2) and adsorbed NH_3 , rather than proceeding through adsorbed nitrate intermediates, aligning with the characteristics of the Eley-Rideal (E-R) reaction mechanism.

Considering the spectral changes under both pre-adsorption conditions, the NH_3 -SCR reaction on the surface of the $\text{Ce-Co}_{0.025}/\text{TiO}_2$ -SG catalyst exhibited characteristics of both L-H and E-R mechanisms. However, the absence of nitrate intermediates in the $\text{NO}+\text{O}_2$ pre-adsorption experiment further supported the E-R mechanism pathway dominated by direct reaction between gaseous NO_x and adsorbed NH_3 .

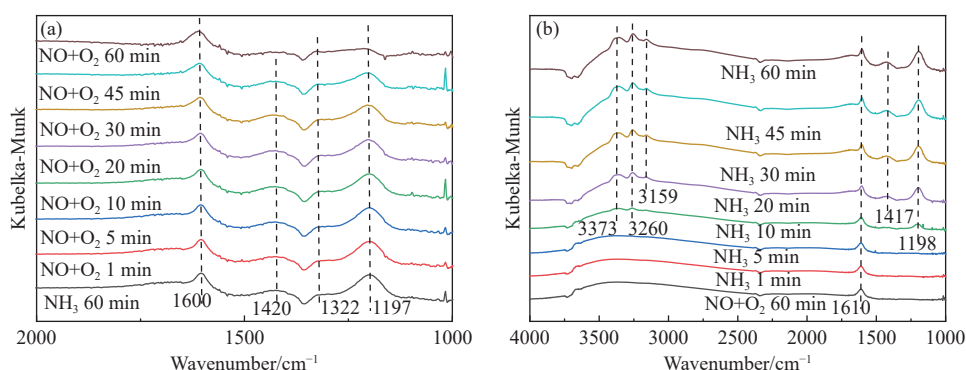


Fig. 10 *In situ* DRIFTS spectra of reaction between $\text{NO} + \text{O}_2$ and pre-adsorbed NH_3 (a), NH_3 and pre-adsorbed $\text{NO} + \text{O}_2$ (b) on $\text{Ce-Co}_{0.025}/\text{TiO}_2$ -SG

Reaction condition: $1.0 \times 10^{-3}\text{ NO}$, $1.0 \times 10^{-3}\text{ NH}_3$, $5\%\text{ O}_2$, N_2 as equilibrium gas, space velocity of 60000 h^{-1} , $200\text{ }^\circ\text{C}$.

3 Conclusions

This study focused on Co-modified Ce/TiO_2 catalysts, systematically investigating the effects of preparation methods and Co loading on their medium-to-low temperature denitrification performance. After screening the optimal doping ratio, the structure-activity relationship was

revealed by combining physicochemical characterization and mechanistic analysis. Performance test results indicated that when using the sol-gel method with a Co/Ti ratio of 0.025, the catalyst maintained over 95% NO conversion in the $225\text{--}350\text{ }^\circ\text{C}$ range and exhibited excellent N_2 selectivity. Its high surface chemisorbed oxygen, abundant Ce^{3+} , and more acidic sites created conditions for enhanced low-temperature activity. Characterization results showed

that the Ce-Co_{0.025}/TiO₂-SG catalyst possessed abundant oxygen vacancies, a high Ce³⁺ proportion, the lowest reduction peak temperature in H₂-TPR (indicating excellent reducibility), and a mesoporous structure that increased acidic site exposure, making it more suitable for medium-to-low temperature reactions. *In situ* DRIFTS characterization results demonstrated that the Ce-Co_{0.025}/TiO₂-SG catalyst follows the Eley-Rideal (E-R) reaction mechanism, effectively inhibiting the formation of nitrate intermediates and exhibiting efficient NO→NO₂ oxidation performance, making it a superior choice for medium-to-low temperature SCR denitrification.

Declaration of Competing Interest

The authors declare no conflict of interest.

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制备方法对 Co 改性 Ce/TiO₂ 催化剂 NH₃-SCR 脱硝性能的影响

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摘 要: 本研究开展了 Co 改性 Ce/TiO₂ 催化剂的制备优化与性能研究, 重点考察了制备方法 & Co 负载量对催化剂低温脱硝活性的调控作用。通过条件筛选确定最优制备参数后, 采用 BET、XRD、XPS、H₂-TPR 及原位 DRIFTS 等多表征技术, 对催化剂的物理化学特性与反应机理展开深入解析。结果表明, 相较于浸渍法与共沉淀法, 以溶胶-凝胶法制备且 Co/Ti 质量比为 0.025 的 Ce-Co_{0.025}/TiO₂-SG 催化剂表现出更优的脱硝活性——在 225–350 °C 下 NO 转化率稳定维持在 95% 以上, 且具有较高的 N₂ 选择性。表征分析表明, 该催化剂表面丰富的氧空位、较高的 Ce³⁺物种占比及较为突出的酸性位点, 共同促进了其低温脱硝性能的提升。本工作为开发高效低温脱硝催化剂提供参考价值。

关键词: 制备方法; Co; Ce/TiO₂; 低温脱硝; NH₃-SCR

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