

Influence of Si/Al ratio of MFI zeolites on the microstructure and catalytic performance of Co-based catalyst for N₂O decomposition

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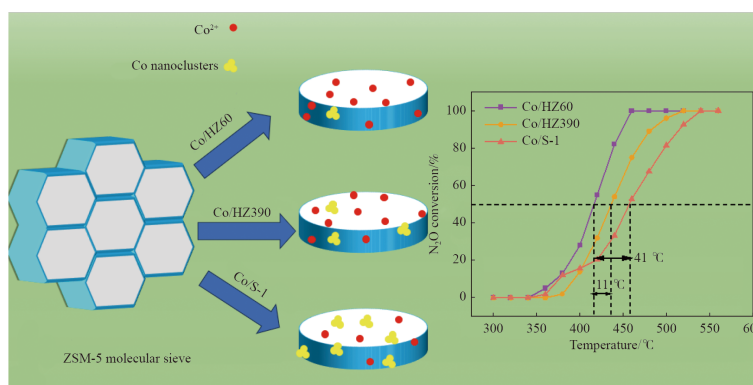
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Abstract: A series of Co-based molecular sieve catalysts with different Si/Al ratios was prepared by the impregnation method. The microstructure properties of Co active sites were finely characterized by means of XRD, TEM, Raman, H₂-TPR, Py-FTIR and XPS technology. The results show that the surface Co species mainly exist in the form of CoO_x nanoclusters and isolated Co²⁺, and the latter exhibits better N₂O decomposition activity. Decreasing the Si/Al ratio of the MFI zeolite promotes the generation of isolated Co²⁺ active sites, thereby enhancing the catalytic activity. Compared with the Co/S-1 catalyst with pure silicon S-1 carrier, the Co/HZ60 with a low Si/Al ratio of ZSM-5 carrier reduces the temperature required for complete N₂O

decomposition by 80 °C, and it shows excellent resistance to O₂ and NO.

Key words: zeolite; Si/Al ratio; Isolated Co²⁺; N₂O decomposition



N₂O is one of the atmospheric pollutant gases, which can induce meteorological disasters, such as photochemical smog, acid rain and haze, and damage the ozone protective layer, causing great harm to the environment^[1]. In addition, N₂O is also a strong greenhouse gas, its latent heat of heating per molecule is about 265 times that of CO₂^[2]. Agricultural fertilization, fossil fuel combustion, and chemical production processes such as nitric acid and adipic acid are the main anthropogenic sources of N₂O emissions^[3–4]. Under the impetus of the national “dual carbon” policy, it is imperative to promote pollution control and carbon emission in the nitric acid and adipic acid production process. Direct catalytic decomposition technology, with its

advantages of simplicity, low cost, high efficiency and no secondary pollution, is regarded as the most ideal method for reducing N₂O emissions at present. Noble metal catalysts, metal oxide catalysts and molecular sieve catalysts are the three mainstream types of N₂O direct decomposition catalysts^[5–7]. However, although precious metal and metal oxide catalysts show high catalytic performance at relatively low temperatures, their activity is severely affected by impurity gases such as NO_x, O₂ and H₂O. Additionally, the high cost of precious metals hinders their large-scale industrial application^[8–10]. In contrast, molecular sieve catalysts loaded with transition metals have regular channels and stable active sites, which can

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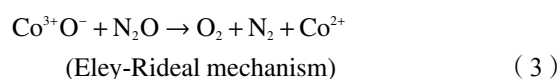
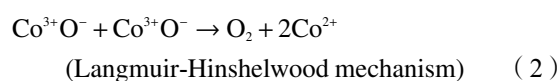
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effectively suppress the influence of impurity gases and showing great application potential in N₂O catalytic decomposition reactions^[11–12].

It was reported that the metal ions anchored on the surface of the molecular sieve carrier are the main active centers for N₂O catalytic decomposition, and the reaction process involves redox cycles of metal ions. Taking ion-exchanged Co/ZSM-5 as an example, the reaction proceeds as follows: N₂O molecules adsorb on Co²⁺ sites, oxidizing them to Co³⁺ while cleaving the N–O bond to release N₂ and form Co³⁺O species (Eq.(1)). After that, two Co³⁺O[–] species migrate and recombine on the surface of the catalyst desorbing O₂ and reducing back to Co²⁺, (Langmuir-Hinshelwood mechanism, Eq.(2)). In addition, Co³⁺O[–] species can also react with another gas-phase N₂O molecules facilitating N–O bond cleavage to yield N₂ and O₂ while reducing Co³⁺ to Co²⁺ (Eley-Rideal mechanism, Eq.(3))^[13–14]. Among them, the O₂ desorption process (Eq.(2) and Eq.(3)) is regarded as the rate-controlling step of the reaction^[15].



The microscopic electronic structure of Co active species and their distribution in molecular sieve carriers are important factors affecting their catalytic activity, which is closely related to the structural properties of the molecular sieve carrier itself and the method of Co species incorporation^[16–18]. Shortening the pore length of zeolite and increasing their specific surface area are conducive to the dispersion of active Co species, thereby enhancing their contact with N₂O molecules and improving catalytic activity^[19]. Ghahri et al.^[20] found that the acid treatment of zeolite could significantly increase their specific surface area and inhibit the agglomeration of cobalt species, which significantly enhanced the N₂O decomposition performance. Kang et al.^[17] found that the three-dimensional pore structure of the ZSM-5 is more conducive to the dispersion of Co species than that of ZSM-23 with a one-dimensional ten-membered ring pore structure. The experimental result showed that the catalytic activity of Co/ZSM-5 for N₂O decomposition is almost twice that of the Co/ZSM-23 catalyst under the reaction conditions of 450 °C, 30% N₂O and GHSV = 30000 h^{–1}. Zhang et al.^[21] regulated the distribution of Al atoms in the ZSM-5 skeleton by modulating the silicon and aluminum sources in the synthesis system, and found that Co²⁺ located in sinusoidal channels was more active than that located in straight or intersection channels and formation of smaller, highly dispersed Co active sites. Dong et al.^[22] reported that the type of cobalt source significantly affects the physicochemical properties of Co species and their catalytic

performance for N₂O decomposition. Compared with cobalt nitrate and cobalt acetate, using cobalt chloride as the cobalt source is more conducive to the generation of Co²⁺ and the decomposition of N₂O. Because of the skeleton Al atom is the main anchoring site for alien Co species, the Si/Al ratio of zeolite significantly affects the microstructure of Co species and their catalytic performance for N₂O decomposition^[23–25]. Zhai et al.^[16] found that a higher Si/Al ratio of ZSM-5 was conducive to the generation of highly dispersed Co²⁺ species. Grzybek et al.^[26] found that Co species on ZSM-5 with a high Si/Al ratio exhibit higher reducibility, while those on ZSM-5 with a low Si/Al ratio tend to migrate and form larger oxide particles, which are difficult to reduce completely.

Although there are numerous reports on the catalytic N₂O decomposition reaction of Co-based molecular sieve catalysts at present, most of the research focuses on the influence of the structural properties of the zeolite themselves (such as pore structure, aluminum content and distribution) on the catalytic activity. There is still a lack of understanding of influence of Co structure on the catalytic performance of the molecular sieve carrier. In fact, Co species can exist on molecular sieve carriers in various forms, such as isolated Co²⁺, CoO_x clusters and Co₃O₄ nanoparticles^[27]. These Co species exhibit distinct electronic structure characteristics and adsorption properties for N₂O molecules. Revealing the structure-activity relationship between these Co species and their performance for N₂O decomposition is of great significance for a deeper understanding of the microscopic mechanism of Co-based molecular sieve catalysts on N₂O catalytic decomposition.

In this work, a series of Co/HZSM-5 catalysts were prepared by the impregnation method to catalyze N₂O decomposition. The microstructure of the Co species was modulated by varying the Si/Al ratio of the HZSM-5 support while maintaining a constant Co loading. The physicochemical information of the catalyst was precisely characterized by TEM, XRD, Raman, H₂-TPR, Py-FTIR and XPS to investigate the influence of the HZSM-5 Si/Al ratio on the microstructure of surface Co species. Combining with the results of performance evaluation and *in situ* infrared characterization, the influence of the kinds of Co species on N₂O catalyzing decomposition were analyzed. This work can provide a reference for the design and development of high-performance N₂O decomposition catalysts and a deeper understanding of their reaction mechanisms.

1 Experimental

1.1 Preparation of catalysts

HZSM-5 molecular sieve carriers with different Si/Al ratios were prepared by the seed-induced hydrothermal crystallization method. Specifically, amount of sodium hydroxide (NaOH), tetrapropyl ammonium hydroxide

(TPAOH) and deionized water were mixed in a beaker and stirred thoroughly. Then ethyl orthosilicate (TEOS) was added into above mixture drop by drop. After stirring for 24 h, it was transported to a crystallization reactor and crystallized at 170 °C for 24 h to obtain the crystal seeds. Then, a certain amount of obtained seed crystals was added to the ZSM-5 molecular sieve growth feed solution. The molar composition of the feed solution was 4.4 TPAOH:0.1 Na₂O:25 SiO₂:0.04 Al₂O₃:1048 H₂O:100 ETOH. Further continuous stirring for 3 h, it was crystallized in the crystallization reactor at 210 °C for 3 h. The obtained crystallization product was centrifuged and washed repeatedly with deionized water until the supernatant reached pH value 7.0, dried at 100 °C, and calcined at 550 °C for 6 h. Subsequently, the sample was subjected to ion exchange with a 0.80 mol/L NH₄Cl aqueous solution. After drying and calcination, the H-type ZSM-5 molecular sieve was obtained and named HZ-*X* (*X* is the Si/Al ratio of the HZSM-5 carrier). Finally, 0.335 g of cobalt nitrate hexahydrate was dissolved in 4 g of deionized water, and the resulting solution was dropwise added to 5 g of the HZ-*X* support. The mixture was ultrasonicated for 30 min, allowed to stand at room temperature for 4 h, dried at 100 °C for 6 h, and finally calcined at 500 °C for 4 h, yielding the Co/HZSM-5 catalysts with different Si/Al ratios, which were denoted as Co/HZ-*X*.

1.2 Characterization

The X-Ray powder diffraction (XRD) tests were conducted on the SmartLab9 X-ray diffractometer equipped with Cu K α rays as the radiation source. The scanning range and scanning speed for the XRD test were 5°–70° and 2(°)/min, respectively. The X-ray fluorescence (XRF) was carried out on a ZSX Primus II spectrometer equipped with a 4 kW Rh target X-ray tube to analyze the elemental composition of the samples. The texture properties of samples were tested by N₂ physical adsorption technology on an ASAP 2020 physical adsorption instrument. The test samples were degassed under vacuum conditions at 250 °C for 4 h, and the isotherms were measured at –196 °C. The morphology of samples was tested using the HT7800 transmission electron microscope, and the pressurized voltage selected for the test is 200 kV. The Raman spectra were measured on the Horiba LabRAM HR Evolution Raman spectrometer. A 532 nm laser light source with a laser power of 10 mW was selected during the test, and the spectral resolution was 1 cm^{–1}. The PHI Genesis X-ray photoelectron spectrometer equipped with an Al K α ray source was adopted for XPS testing. The binding energy (BE) value was calibrated with a C 1s signal of 284.8 eV. The analysis of H₂-TPR and NH₃-TPD was carried out on the Micromeritics AutoChemII 2920 analyzer. During the H₂-TPR test, the sample was pretreated at a temperature of 300 °C for 1 h, and then a mixture of 10% H₂/Ar was purged when the temperature cooled to 50 °C. The H₂-TPD curve was recorded as the temperature was raised to 700 °C

at a rate of 10 °C/min. As for NH₃-TPD, the sample was pretreated at 550 °C for 1 h to clean the surface, then 5% NH₃/He mixed gas was introduced when the temperature decreased to 100 °C. The physically adsorbed ammonia was removed by a He flow. The NH₃-TPD spectrum was recorded by a TCD detector as the temperature increased from 100 to 550 °C at a rate of 10 °C/min in a He atmosphere. The Py-FTIR testing was conducted on the Bruker Tensor 27 infrared spectrometer. Before the test, the impurity gas on sample was removed at 400 °C under a vacuum atmosphere. Then, pyridine is introduced and adsorbed for 10 min, followed by vacuuming at 200 °C to remove the weakly adsorbed pyridine molecule. When the temperature cooled to room temperature, the Py-FTIR spectra were recorded. The *in situ* infrared experiment was conducted on the Nicolet iS50 Fourier Transform infrared spectrometer. The catalyst was pre-treated in N₂ at 500 °C for 1 h. After reducing the temperature to 150 °C, 0.1% N₂O/He is introduced at a flow rate of 30 mL/min. After stabilizing for 10 min, the temperature is increased to 400 °C at a rate of 2 °C/min. The spectrum was recorded at the wavenumber acquisition range of 400–4000 cm^{–1}, and the spectral resolution was set at 4 cm^{–1}. The spectrum at the same temperature without the introduction of raw gas as the background.

1.3 Performance evaluation

The N₂O catalytic decomposition performance for the prepared catalysts was evaluated in a micro-fixed-bed reactor. Before the test, the catalyst was first pressed into tablets, then crushed and sieved into particles of 40–60 mesh. 0.3 g of catalyst was packed into the reactor. After increasing the temperature to 280 °C, 0.1% N₂O/He was introduced with the space velocity of 10000 h^{–1}. For every 20 °C increase, the concentration of N₂O in the reaction tail gas was detected by gas chromatography (GC) equipped with a TCD detector. The calculation formula for N₂O conversion is shown below:

$$x = \frac{c_{in} - c_{out}}{c_{in}} \times 100\% \quad (4)$$

Herein, *x* represents the conversion rate of N₂O, *c*_{in} refer to the N₂O concentration at the inlet of the reactor, and *c*_{out} are the N₂O concentration at the outlet of the reactor.

2 Results and discussion

2.1 Characterization of physical properties

The actual Si/Al ratio of the prepared molecular sieve carrier was tested by X-ray fluorescence spectrometry (XRF), and the results are listed in Table 1. Apparently, the actual Si/Al ratios of HZ60 and HZ390 molecular sieve carriers are 35 and 164, lower than the corresponding feed Si/Al of 60 and 390, respectively.

Table 1 The SiO₂/Al₂O₃ ratios and structure parameters for carriers and catalysts

Sample	SiO ₂ /Al ₂ O ₃ ratio	Total surface areas/(m ² ·g ⁻¹)	Total pore volumes/(cm ³ ·g ⁻¹)
HZ60	35	486	0.272
HZ390	164	569	0.284
S-1	700	509	0.261
Co/HZ60		389	0.261
Co/HZ390		384	0.188
Co/S-1		435	0.219

This is because the alkali-mediated desilication occurred during the strongly alkaline and relatively high-temperature synthetic environment, which reduced the actual Si/Al ratio of the molecular sieve. As for the S-1 molecular sieve carrier, although no aluminum source was added during its synthesis process, the actual Si/Al ratio detected was 700. This might be caused by the trace aluminum impurities inherent in the template agent and the silicon source, combined with the trace aluminum species remaining in the inner lining of the reaction vessel. After treating the HZ60 molecular sieve with 2 mol/L nitric acid, the Si/Al ratio significantly increased from 35 to 85, indicating that some of the framework aluminum had been etched by the acid.

Figure 1 shows the XRD patterns of the Co/HZ60, Co/HZ390 and Co/S-1 catalysts. It can be seen that diffraction peaks belonging to MFI zeolite appeared in all samples at 2θ angles of 7° – 9° and 23° – 25° , indicating that the impregnation process of Co precursors did not damage the framework structure of the zeolite^[16]. Meanwhile, no diffraction peaks belonging to CoO or Co₃O₄ were observed in the XRD patterns, suggesting that the Co species were highly dispersed on the surface of MFI molecular sieve carriers with different Si/Al ratios, and their grain sizes were below the XRD detection limit^[28].

Figure 2(a)–(c) shows the TEM images of S-1, HZ390 and HZ60 zeolite. All the samples presented a cubic structural morphology. Unlike HZ390 and S-1 samples, a unique structure accumulated by tiny grains can be observed around the cubic grains of HZ60, which indicates that excessively increasing the aluminum species in the synthesis liquid system is harmful to the epitaxial growth of the molecular sieve skeleton structure.

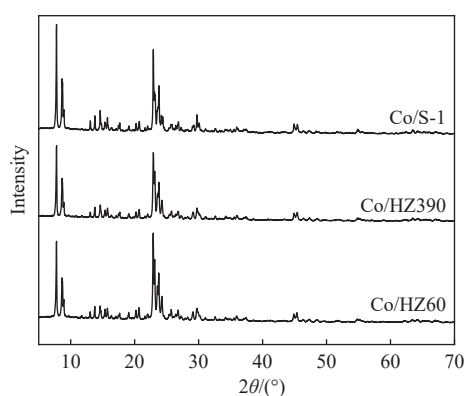


Fig. 1 XRD patterns for Co/HZ60, Co/HZ390 and Co/S-1 catalysts

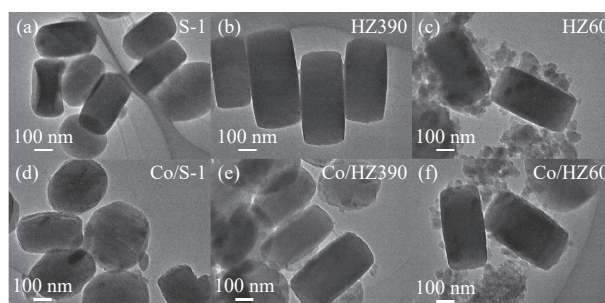


Fig. 2 TEM images of S-1, HZ60 and HZ390 carriers and Co/HZ60, Co/HZ390 and Co/S-1 catalysts

After impregnating Co species, the Co/HZ60, Co/HZ390 and Co/S-1 catalysts exhibited a cubic morphology which was similar to that of the carriers, but the edges of grains became rougher and some irregular attachments were formed on the surfaces (Figure 2(d)–(f)). Compared with Co/S-1 and Co/HZ390 catalysts, the surface of Co/HZ60 grains possessed more tiny attachments. Despite this, no obvious Co₃O₄ nanoparticles were observed on the surface of all Co-based molecular sieve catalysts, which suggested that the introduced Co species were highly dispersed on the catalyst surface. These results were consistent with the XRD results.

The texture properties of the prepared samples were characterized by N₂ physical adsorption-desorption technology. As shown in Figure 3(a), the HZ60, HZ390 and S-1 carriers exhibit type I isothermal curves, suggesting the microporous structures for molecular sieve carriers. Among them, the HZ60 carrier shows an H4 type hysteresis loop at $0.8 < p/p_0 < 1.0$, indicating the existence of a mesoporous structure. These mesoporous pores might be formed by the accumulation of tiny attachments on the surface of HZ60 grains. The Co/HZ60, Co/HZ390 and Co/S-1 catalysts exhibited type I isothermal curves similar to the corresponding carriers. However, unlike the HZ60 carrier, no hysteresis loop structure was observed in the isotherms of the Co/HZ60 catalyst, indicating that the introduced Co species blocked the surface mesoporous structure. The texture properties of the catalyst are listed in Table 1. Compared with HZ60, HZ390 and S-1 carriers, the total specific surface area of Co/HZ60, Co/HZ390 and Co/S-1 catalysts decreased from 486, 569 and 509 m²/g to 389, 384 and 435 m²/g, respectively. And the total pore volumes of Co/HZ60, Co/HZ390 and Co/S-1 catalyst decreased from 0.272, 0.284 and 0.261 cm³/g of HZ60, HZ390 and S-1 to 0.261, 0.188 and 0.219 cm³/g, respectively. These results indicated that the introduction of Co species blocked the pore structure of the molecular sieve carrier to some extent.

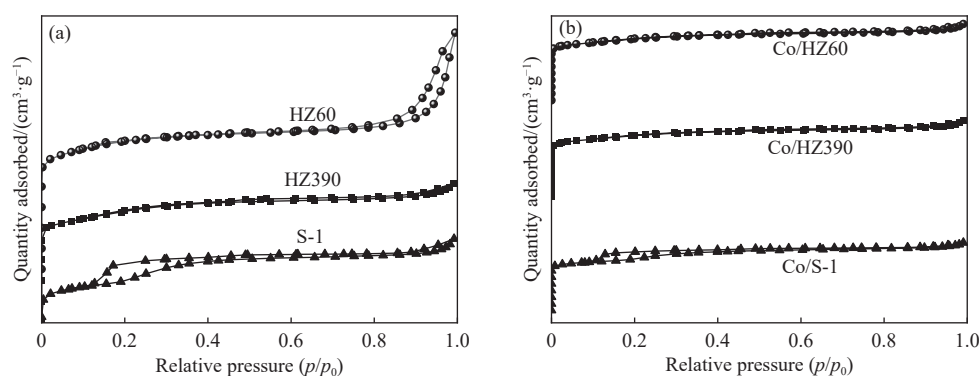


Fig. 3 N₂ physical adsorption-desorption curves for carriers and catalysts with different Si/Al ratios

2.2 Characterization of Co species

The Raman spectroscopy was used to characterize the properties of Co species on the surface of molecular sieve carriers with different Si/Al ratios. As shown in Figure 4(a), no obvious Raman peak was observed in the spectrum of the Co/HZ60 catalyst, while the Co/HZ390 catalyst exhibited a symmetrical vibrational peak belonging to the octahedral CoO₆ species at 683 cm⁻¹ [29]. The Co/S-1 catalyst exhibited other symmetrical vibrational peaks at 477 and 517 cm⁻¹, which belonged to the tetrahedral CoO₄ species [30]. This result indicates that the Co species existed in the form of oxides on the zeolite with high Si/Al ratios (such as Co/HZ390 and Co/S-1). The reduction properties of Co species on the catalyst were further characterized by H₂-TPR. As the H₂-TPR curves shown in Figure 4(b), the Co/HZ60, Co/HZ390 and Co/S-1 catalysts present two H₂ reduction peaks at 350–500 °C. The peaks located near

415.5 and 460 °C are attributed to the reduction processes of Co³⁺ → Co²⁺ and Co²⁺ → Co⁰, respectively [31–32]. These results revealed the presence of cobalt oxide on all catalysts. The similar H₂ reduction temperatures of cobalt oxides in the three catalysts suggested that the Si/Al ratio of the molecular sieve has a relatively low influence on the reduction performance of surface cobalt oxides. However, the peak area of H₂ reduction decreases significantly with the reduction of the Si/Al ratio of molecular sieve carriers. The H₂ consumption calculated based on the reduction peak area is shown in Table 2. The hydrogen consumption of Co/HZ390 catalyst decreased from 570 μmol/g of Co/S-1 to 390 μmol/g, and Co/HZ60 sharply reduced to 100 μmol/g. These results indicate that the cobalt oxide content for different catalysts decreases with the reduction of the Si/Al ratio. Considering the same load amount of Co species, it can be found that there are other forms of Co species present on these catalysts with different Si/Al ratios.

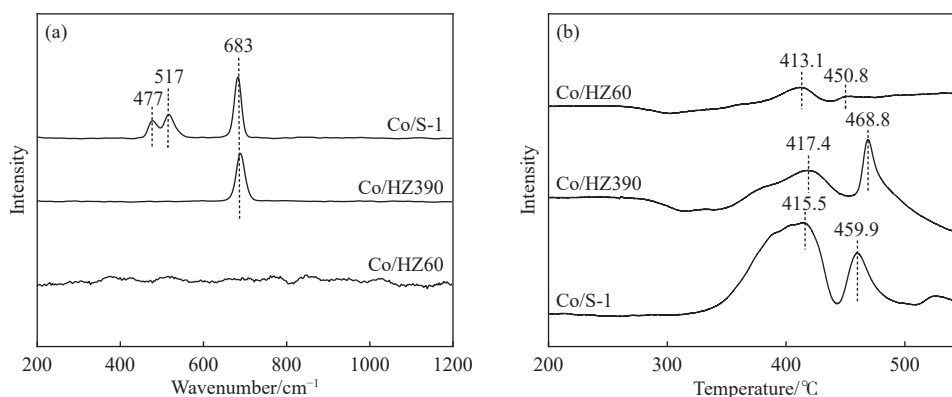


Fig. 4 (a) Raman spectra and (b) H₂-TPR profiles of Co/HZ60, Co/HZ390 and Co/S-1 catalysts

Table 2 H₂ consumption and total acid amount of catalysts with different Si/Al ratios

Catalyst	H ₂ consumption/(μmol·g ⁻¹)	Acid amount/(μmol·g ⁻¹)		Total acid amount/(μmol·g ⁻¹)
		Brønsted	Lewis	
Co/HZ60	100	45.1	44.3	800
Co/HZ390	390	2.1	12.6	500
Co/S-1	570	—	—	120
HZ60	—	71.7	37.7	740
HZ390	—	24.5	6.7	480
S-1	—	—	—	104

The effect of Co species loading on the surface acidity of the zeolite was investigated by NH_3 -TPD. As shown in Figure 5(a), three NH_3 desorption peaks can be observed in the NH_3 -TPD curves of HZ60 and HZ390 samples. The NH_3 desorption peaks observed in the ranges of 100–170, 200–260 and 400–500 °C are attributed to weak acid, moderate-strength acid, and strong acid sites, respectively. Different from that of HZ60 and HZ390, the S-1 carrier only showed a weak NH_3 desorption peak at about 130 °C, suggesting that the acid sites on its surface were mainly weak acids. After the introduction of the Co species, the NH_3 desorption peaks at 400–500 °C disappeared for Co/HZ60 and Co/HZ390 catalysts, while the peak at 135 °C was significantly enhanced. This indicated that the introduced Co species primarily interacted with the strong acid sites on the zeolite support surface and generated new weak acid sites. As for the Co/S-1 catalyst, it showed a similar NH_3 desorption peak to that of the S-1 carrier at about 125 °C. Based on the integration of the area of the NH_3 desorption peak, the acid content of catalysts with different Si/Al ratios was calculated (Table 2). Because the high aluminum content of the HZ60 carrier, its total acid content can reach 800 $\mu\text{mol/g}$, while the HZ390 carrier with low aluminum content has a total acid content of 500 $\mu\text{mol/g}$. The total acid content of the S-1 carrier is the least, only 120 $\mu\text{mol/g}$. Due to the shielding effect of Co species on acid sites, the total acid contents of Co/HZ60, Co/HZ390 and Co/S-1 catalysts slightly decreased compared with the corresponding carriers, which were 740, 480 and 104 $\mu\text{mol/g}$,

respectively.

The acid structure of the molecular sieve carrier and the corresponding catalyst were further analyzed by Py-FTIR, and the test results were shown in Figure 6. The peaks located at 1450 and 1550 cm^{-1} in the spectrum belong to the infrared absorption peaks of pyridine molecules on Lewis acid (L-acid) and Brønsted acid (B-acid) sites, respectively^[33]. Because of the high amount of acid sites, the infrared absorption peaks of the HZ60 carrier at 1450 and 1550 cm^{-1} are significantly greater than those of the HZ390 carrier. No distinct infrared peaks were observed in the range of 1400–1600 cm^{-1} for the purely siliceous S-1, indicating the absence of acidic sites on its surface. This is because the Brønsted and Lewis acidities in HZSM-5 zeolite originate from tetrahedrally coordinated framework aluminum and extra-framework aluminum species, respectively^[33]. Compared with the HZ60 and HZ390 carriers, the infrared peaks of the Co/HZ60 and Co/HZ390 catalysts at 1550 cm^{-1} were significantly weakened, while the infrared peaks at 1450 cm^{-1} were apparently enhanced (Figure 6(b)). This was because the introduced Co species can react with B acid sites and convert them into L acid sites (isolated Co^{2+})^[27]. No obvious infrared peak was observed in the range of 1400–1600 cm^{-1} for the S-1 carrier and Co/S-1 catalyst due to the lack of acidic sites. The acid content of B acid sites and L acid sites was listed in Table 2. HZ60 has the highest amounts of B acid and L acid, which reached up to 71.7 and 37.7 $\mu\text{mol/g}$ respectively.

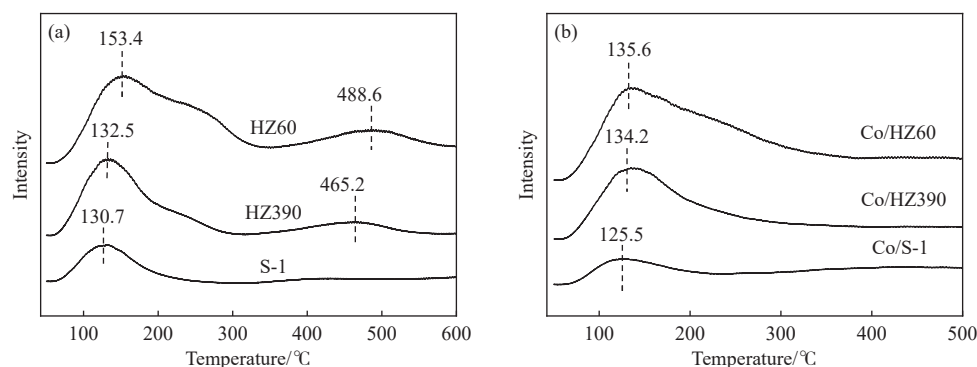


Fig. 5 NH_3 -TPD curves for carriers and catalysts with different Si/Al ratios

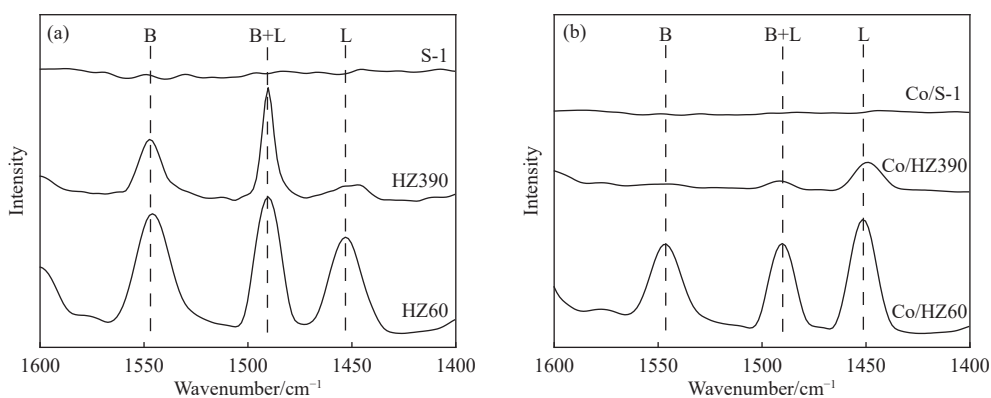


Fig. 6 Pyridine-FTIR spectra of (a) S-1, HZ390 and HZ60 carriers and (b) the corresponding Co-based catalysts

The amounts of B acid and L acid in the HZ390 catalyst were reduced to 24.5 and 6.7 $\mu\text{mol/g}$, respectively. After impregnating the Co species, the amounts of B acid in Co/HZ60 and Co/HZ390 decreased significantly to 45.1 and 2.1 $\mu\text{mol/g}$, respectively, while the amounts of L acid increased to 44.3 and 12.6 $\mu\text{mol/g}$, respectively. These results indicated that isolated Co^{2+} species exist in both Co/HZ60 and Co/HZ390 catalysts.

The oxygen species in Co/HZ60, Co/HZ390 and Co/S-1 catalysts were characterized by XPS. The results are shown in Figure 7(a). A large peak could be observed between 529–537 eV for Co/HZ60, Co/HZ390 and Co/S-1 catalysts. Among them, the signal peak at 532.9 eV (O_α) was attributed to the skeleton oxygen species of the molecular sieve carrier, while the peaks at about 531.0 eV (O_β) and 534.5 eV (O_γ) are attributed to the lattice oxygen species of the CoO_x species and surface hydroxyl oxygen species, respectively^[22]. Based on the integration of peak areas, the relative contents of each oxygen species on the catalyst surface were calculated, and the results are listed in Table 3. Because the zeolite is mainly composed of tetrahedral silicon-oxygen species, the oxygen species in their framework are the main oxygen species of Co-based molecular sieve catalysts, which account for 92.2%, 86.9% and 88.3% for Co/HZ60, Co/HZ390 and Co/S-1 catalysts, respectively. Correspondingly, the relative content of lattice oxygen species associated with CoO_x species increased with the increasing Si/Al ratio of the zeolite. Compared with the Co/HZ60 catalyst, the lattice oxygen content (O_β) in the Co/HZ390 and Co/S-1 catalysts increased from 3.6% to 5.5% and 5.9%, respectively, and the $\text{O}_\beta/\text{O}_\alpha$ ratio also

increased from 0.04 to 0.06 and 0.07, respectively. This indicated that increasing the Si/Al ratio of the molecular sieve carrier can promote the generation of more CoO_x species, which is consistent with the characterization results of H_2 -TPR.

It can be seen from the Co $2p_{3/2}$ XPS spectrum that three distinct signal peaks were observed at 792.50–776.40 eV for the Co/HZ60, Co/HZ390 and Co/S-1 catalysts (Figure 7 (b)). Specifically, the signal peaks located at approximately 782.00 and 784.65 eV (for Co/HZ60 and Co/HZ390) are attributed to Co^{3+} and Co^{2+} , respectively, while the peak at about 787.50 eV corresponds to the satellite peak of Co^{2+} ^[34–35]. However, the binding energies of Co^{2+} and Co^{3+} in the Co/S-1 catalyst were noticeably lower than those of the other samples, shifting down to 784.12 and 781.31 eV, respectively. This suggested that the Co species of the Co/S-1 catalyst presented a relatively higher electron cloud density than that of Co/HZ60 and Co/HZ390 catalysts. The relative contents of Co^{2+} and Co^{3+} of each catalyst are listed in Table 4. Among them, the Co/HZ60 catalyst possessed the highest $\text{Co}^{2+}/\text{Co}^{3+}$ ratio, which attained 0.79. When the Si/Al ratio of the molecular sieve increased to 390, the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio of Co/HZ390 catalyst significantly decreased to 0.66. For the Co/S-1 catalyst supported on pure silicon molecular sieve carrier, the ratio of Co^{2+} to Co^{3+} was apparently reduced to 0.54. This was because the abundant ion-exchange sites present in low Si/Al ratio zeolite, where the strongly interacting Co^{2+} ions anchored at these sites are less susceptible to oxidation to Co^{3+} .

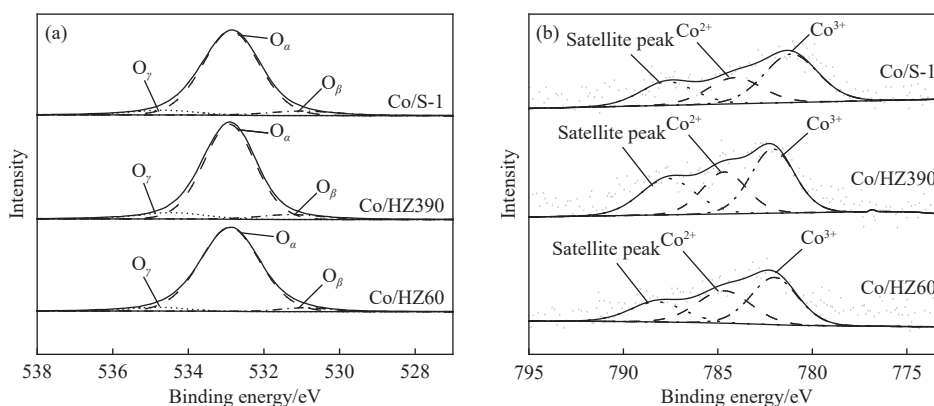


Fig. 7 (a) O 1s and (b) Co $2p_{3/2}$ XPS spectra of Co/HZ60, Co/HZ390 and Co/S-1 catalysts

Table 3 Analysis of different oxygen species in Co/HZ60, Co/HZ390 and Co/S-1 catalysts

Catalyst	O species						O _β /O _α
	O _α		O _β		O _γ		
	E _B /eV	content/%	E _B /eV	content/%	E _B /eV	content/%	
Co/HZ60	532.90	92.2	530.90	3.6	534.82	4.2	0.04
Co/HZ390	532.91	86.9	531.20	5.5	534.45	7.6	0.06
Co/S-1	532.87	88.3	530.97	5.9	534.68	5.8	0.07

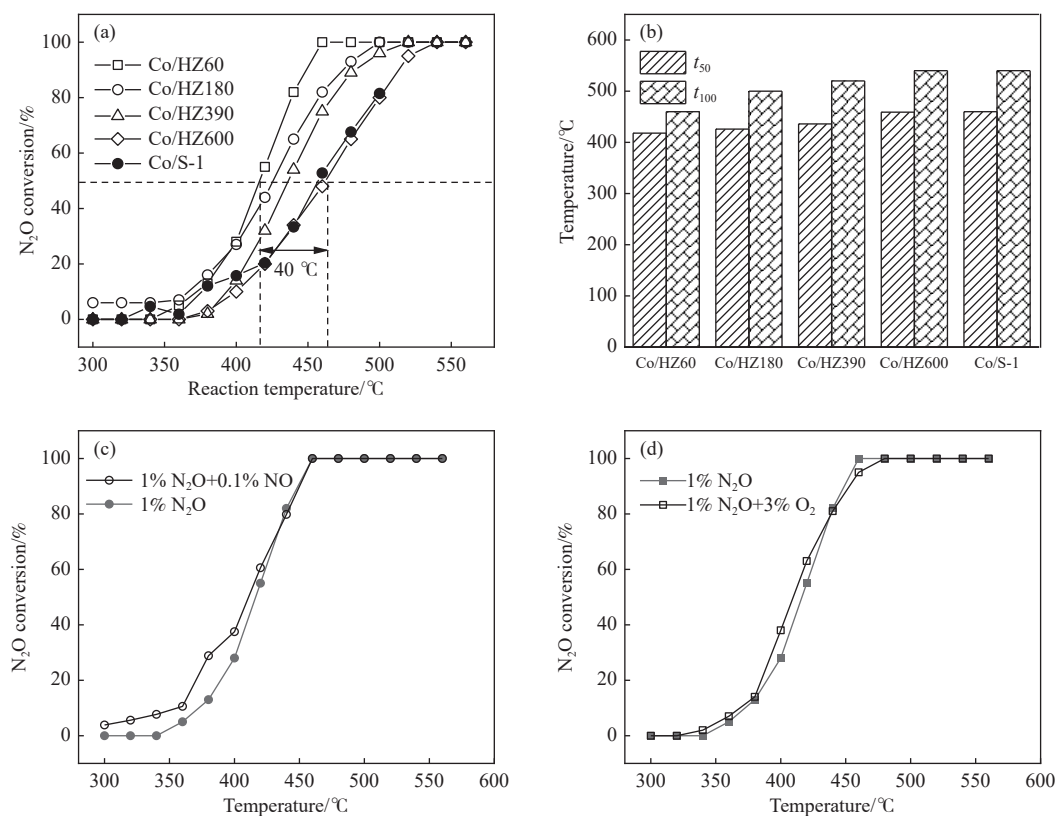
Table 4 Analysis of different Co species in Co/HZ60, Co/HZ390 and Co/S-1 catalysts

Catalyst	Co species				
	Co ²⁺		Co ³⁺		Co ²⁺ /Co ³⁺
	E _B /eV	contents/%	E _B /eV	contents/%	
Co/HZ60	784.65	44.2	781.90	55.8	0.79
Co/HZ390	784.65	39.9	782.00	60.1	0.66
Co/S-1	784.12	35.1	781.31	64.9	0.54

2.3 Evaluation of catalyst activity

Figure 8 shows the N₂O catalytic decomposition performance of Co-based molecular sieve catalysts with different Si/Al ratios. It could be seen from Figure 8(a) that the order of catalytic activity of the prepared catalyst is Co/HZ60 > Co/HZ180 > Co/HZ390 > Co/HZ600 > Co/S-1. Among them, Co/HZ60 exhibited the best catalytic activity, achieving an N₂O decomposition conversion of 55% at 420 °C. When the reaction temperature was raised to 460 °C, complete decomposition of N₂O could be attained. As the Si/Al ratio of the molecular sieve increased from 60 to 180 and 390, the activity of the catalyst declined to a certain extent. At 420 °C, the N₂O decomposition conversion of Co/HZ180 and Co/HZ390 catalysts decreased to 44% and 32%, respectively, while the complete decomposition temperature of N₂O (*t*₁₀₀) significantly increased to 500 °C and 520 °C, respectively (Figure 8(b)). When the Si/Al ratio

was further increased to 600, the Co/HZ600 catalyst exhibited similar N₂O catalytic decomposition activity to that of Co/S-1. The *t*₁₀₀ of Co/HZ600 and Co/S-1 was as high as 540 °C, and the N₂O conversion was only about 20% at 420 °C. These results revealed that reducing the Si/Al ratio of zeolite is conducive to enhancing the catalytic decomposition activity of N₂O. In actual industrial exhaust gases (such as those from the nitric acid industry), apart from N₂O, there are also impurity gases like O₂ and NO^[1]. The performance of resisting impurity gases is an important indicator for evaluating N₂O decomposition catalysts. Figure 8(c) and 8(d) showed the O₂ resistance and NO resistance of the Co/HZ60 catalyst, respectively. It can be seen that when 3.0% O₂ and 0.1% NO were respectively introduced into the reaction gas, the *t*₅₀ and *t*₁₀₀ of the Co/HZ60 did not show a significant decrease, indicating a good impurity resistance for Co/HZ60 catalyst.


Fig. 8 N₂O catalytic performance for different catalysts

2.4 In situ infrared experiment

The *in situ* infrared spectrogram of Co/HZ60 and Co/HZ390 catalysts is shown in Figure 9. The infrared peaks located at 1557 and 1682 cm^{-1} in the spectrum can be attributed to the stretching vibration of the nitro species (*NO_2) and the bending vibration of the nitrosyl group (*NO), respectively. The infrared peak located at 2050–2270 cm^{-1} can be attributed to the antisymmetric stretching vibration of gaseous N_2O ^[36–37]. It is generally believed that there are two adsorption activation methods for N_2O molecules. One type is adsorbed on the metal active site through the oxygen terminal, which tends to break the N–O bond and generate N_2 and surface-adsorbed oxygen *O species. Another type tends to generate NO and *N species through nitrogen terminal adsorption, which breaks the N–N bond. The generated NO can combine with surface-adsorbed *O species to form nitro species^[37–38]. Therefore, whether N_2O molecules have decomposed can be analyzed by the species of nitro or nitrosyl groups on the surface of the catalyst. As shown in Figure 9(a) and (b), the Co/HZ60 catalyst exhibited distinct nitro or nitrosyl species at 250 °C, indicating the onset of N_2O decomposition at this temperature. However, the obvious peaks attributed to nitro or nitrosyl species appeared at 350 °C for the Co/HZ390 catalyst (Figure 9(c) and (d)). This phenomenon indicated that the Co species on zeolite carrier with a low Si/Al ratio presented higher catalytic activity for N_2O decomposition.

2.5 Discussion

For transition metal-molecular sieve catalysts, the introduced metal species can exist in the form of cations, metal-oxygen clusters, and oxide particles. The Raman results show that CoO_x species exist in the Co/HZ390 and Co/S-1 catalysts. The H_2 -TPR results indicate that Co/HZ60, Co/HZ390 and Co/S-1 all exhibited H_2 reduction peaks belonging to the CoO_x species within the range of 350–500 °C. However, no diffraction peaks belonging to CoO or Co_3O_4 are observed in the corresponding XRD patterns, and no obvious cobalt oxide particles are observed in the TEM images either. These results indicate that the cobalt oxides on the catalyst surface are predominantly present as nanoclusters. It can be known from the hydrogen consumption of catalysts that the content of cobalt oxide on the catalyst surface decreases with the reduction of the Si/Al ratio of the molecular sieve carrier. The Py-FTIR characterization shows that the amount of L-acid on the surfaces of Co/HZ60 and Co/HZ390 is significantly higher than that of HZ60 and HZ390 carriers, indicating that more Co species exist in the form of isolated Co^{2+} in the catalyst with a low Si/Al ratio. The Co $2p_{3/2}$ XPS characterization results reveal that the ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ of the catalyst increased from 0.54 of Co/S-1 to 0.66 of Co/HZ390 and further increased to 0.79 of Co/HZ60. It can be seen that the Co species on the surface of the prepared catalyst exist in the form of cobalt oxide clusters and isolated Co^{2+} .

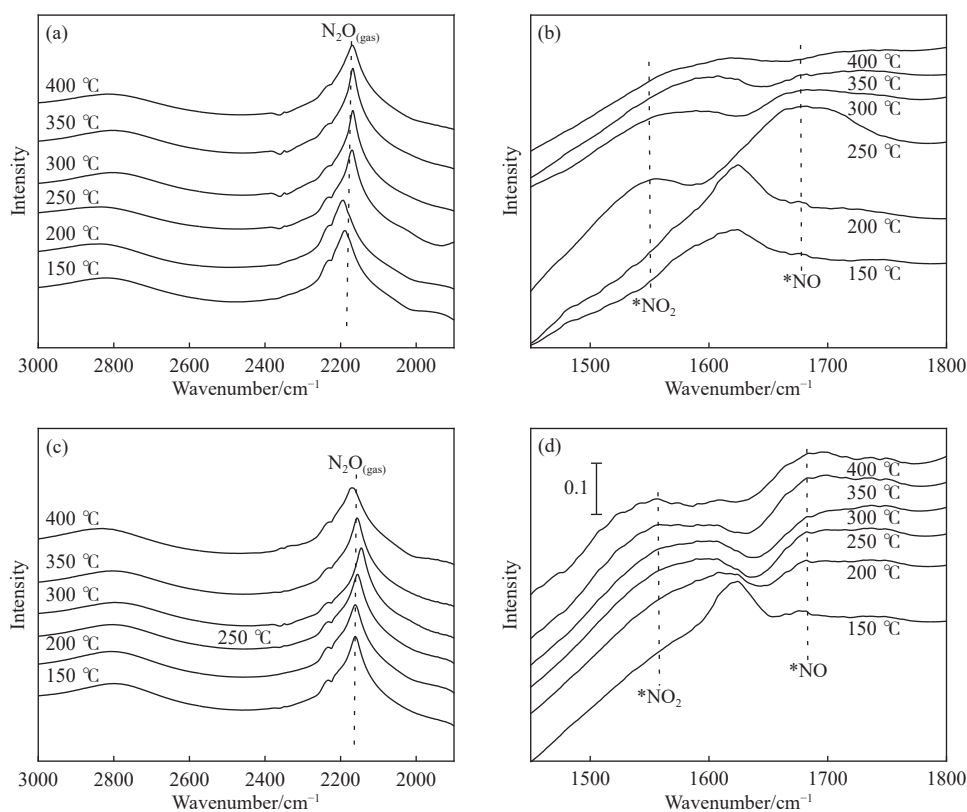


Fig. 9 *In situ* FT-IR spectra for (a), (b) Co/HZ60 and (c), (d) Co/HZ390 catalysts

With a decreasing Si/Al ratio of the zeolite carrier, the proportion of cobalt oxide clusters gradually declines, while the proportion of isolated Co^{2+} gradually increases. The microstructural variation of Co species significantly influences their catalytic activity for N_2O decomposition. The activity evaluation results show that the catalytic activity sequence is $\text{Co}/\text{HZ60} > \text{Co}/\text{HZ390} > \text{Co}/\text{S-1}$, indicating that the catalytic activity of isolated Co^{2+} is higher than that of cobalt oxide clusters. When nitric acid is used to pre-destroy the skeletal Al sites anchored to isolated Co^{2+} , the catalytic activity of $\text{Co}/\text{HZ60}$ decrease significantly. As shown in Figure 10, the t_{50} of the acid-treated sample ($\text{Co}/\text{HZ60}$ -Acid) increased by 12 °C compared to before the treatment ($\text{Co}/\text{HZ60}$), while the t_{100} increased by 40 °C. This experimental result once again proves that the catalytic activity of isolated Co^{2+} on the surface of zeolite is significantly higher than that of cobalt oxide nanoclusters.

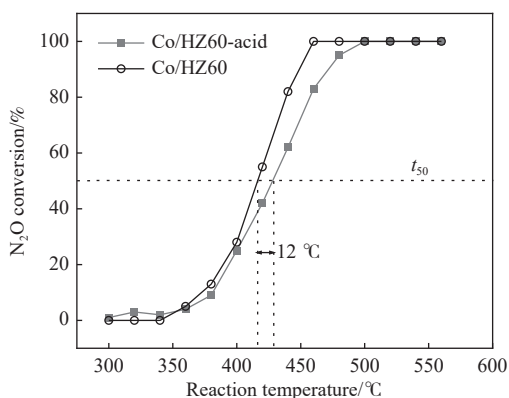


Fig. 10 N_2O decomposition performance of $\text{Co}/\text{HZ60}$ and $\text{Co}/\text{HZ60}$ -acid catalysts before and after acid treatment

3 Conclusion

In this work, a series of Co-based molecular sieve catalysts with different Si/Al ratios was prepared by the impregnation method. The experimental results show that during the impregnation process, the Co precursors do not damage the molecular sieve structure, and the Co species are mainly highly dispersed on the molecular sieve surface in the form of cobalt oxide nanoclusters and isolated Co^{2+} . Under the same Co loading amount, reducing the Si/Al ratio of the molecular sieve is conducive to generating highly active isolated Co^{2+} species. The strong interaction between the molecular sieve carrier and Co^{2+} species effectively inhibits the oxidation of Co^{2+} to Co^{3+} , thereby improving the adsorption and activation capacity of N_2O molecules. Compared to the $\text{Co}/\text{S-1}$ catalyst supported on pure silica, the low Si/Al ratio $\text{Co}/\text{HZ60}$ catalyst, which possesses a greater number of isolated Co^{2+} active sites, reduces the temperature required for complete N_2O decomposition by 80 °C and demonstrates excellent resistance to both O_2 and NO .

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] LI J, FAN X, CHEN L, et al. Research progress on combined removal technology for NO_x and N_2O in tail gas from nitric acid production[J]. Adv Chem Eng, 2023, 42(7): 3770–3779.
- [2] HU X, FENG L, WU R, et al. Preparation of Co_3O_4 catalyst loaded on eggshells and investigation of its N_2O decomposition performance[J]. J Fuel Chem Technol, 2024, 52(5): 707–716.
- [3] ZHUANG Z, GUAN Z, CHEN J, et al. Review of nitrous oxide direct catalytic decomposition and selective catalytic reduction catalysts[J]. Chem Eng J, 2024, 486: 150374.
- [4] AI X, SONG Y, LI C, et al. Performance study of $\text{FeCo}/\text{H}\beta$ molecular sieves for low-temperature decomposition of N_2O [J]. Mod Chem Ind, 2024, 44(1): 140–146.
- [5] LIU X, WANG Y, ZHAO Y. Sr-doped hydroxyapatite loaded with Co_3O_4 for catalysing N_2O decomposition[J]. J Fuel Chem Technol, 2021, 49(8): 1190–1200.
- [6] XU B, GAO C, WANG Y, et al. Fe/β molecular sieve catalysis of N_2O decomposition[J]. Ind Catal, 2018, 26(1): 36–41.
- [7] WANG Y, ZHOU X, WEI X, et al. $\text{Co}/\text{Hydroxyapatite}$ catalysts for N_2O catalytic decomposition: Design of well-defined active sites with geometrical and spacing effects[J]. Mol Catal, 2021, 501: 111370.
- [8] YU H, LI Y, PAN Y, et al. Dy and K double-additive modified Co_3O_4 catalyst with high resistance to NO for catalyzing N_2O decomposition[J]. Chem Eng J, 2025, 504: 159032.
- [9] ABU-ZIED B M, OBALOVA L, PACULTOVA K, et al. An investigation on the N_2O decomposition activity of $\text{Mn}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ nanorods prepared by the thermal decomposition of their oxalate precursors[J]. J Ind Eng Chem, 2021, 93: 279–289.
- [10] XU M, WANG H, OUYANG H, et al. Direct catalytic decomposition of N_2O over bismuth-modified NiO catalysts[J]. J Hazard Mater, 2021, 401: 123334.
- [11] LIU C, KANG R, BIN F, et al. Insights on copper, manganese, and Nickel/ZSM-5 catalytic mechanisms for nitric oxides selective reduction with ammonia[J]. Carbon Resour Convers, 2022, 5: 15–25.
- [12] ZHANG Y, CAO G, YANG X. Advances in de- NO_x methods and catalysts for direct catalytic decomposition of NO [J]. Energy Fuels, 2021, 35: 6443–6464.
- [13] BITURINI N F, SANTOS A P, BATISTA M S. Influence of co-fed gases (O_2 , CO_2 , CH_4 , and H_2O) on the N_2O decomposition over (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts[J]. React Kinet Mech Catal, 2018, 126: 341–352.
- [14] ABU-ZIED B M, SCHWIEGER W, UNGER A. Nitrous oxide decomposition over transition metal exchanged ZSM-5 zeolites prepared by the solid-state ion-exchange method[J].

- Appl Catal B: Environ, 2008, 84: 277–288.
- [15] NOWAKOWSKI L, HUDY C, ZASADA F, et al. N₂O decomposition on singly and doubly (K and Li)-doped Co₃O₄ nanocubes-establishing key factors governing redox behavior of catalysts[J]. J Am Chem Soc, 2024, 146: 24450–24466.
- [16] ZHAI S, SUO Y, SUN M, et al. Boosting propane dehydrogenation performance over the highly dispersed Co(II) sites on ultra-high silica ZSM-5 zeolite[J]. Fuel, 2024, 366: 131429.
- [17] KANG B, ZHANG R, GUO M, et al. Topological aspect of the distribution of Co species and N₂O decomposition performance for Co/zeolite catalysts[J]. Energy Fuels, 2023, 37: 18019–18029.
- [18] GUO H, MIAO C, HUA W, et al. Ethane conversion in the presence of CO₂ over Co-based ZSM-5 zeolite: Co species controlling the reaction pathway[J]. Mol Catal, 2022, 519: 112155.
- [19] XU G, ZHANG P, CHENG J, et al. Coating mesoporous ZSM-5 by microporous silicalite-1 shell: Preparation and enhanced catalytic properties in methane co-aromatization with propane[J]. Microporous Mesoporous Mater, 2022, 330: 111494.
- [20] GHAHRI G, VAFARHOL A, et al. Removal of greenhouse gas (N₂O) by catalytic decomposition on natural clinoptilolite impregnated with cobalt[J]. Int J Environ Res, 2017, 11: 327–337.
- [21] KANG B, LI M, DI Z, et al. Role of Al pairs on effective N₂O decomposition over the ZSM-5 zeolite catalyst[J]. Catal Today, 2023, 402: 17–26.
- [22] DONG H, ZHAO M, CHE J, et al. Influence of cobalt source on the catalytic performance of Co/RPSA catalysts for the decomposition of N₂O[J]. J Fuel Chem Technol, 2025, 53(6): 918–926.
- [23] ZHENG K, WANG Y, HU X, et al. Effect of reduction-oxidation pretreatment on the catalytic performance of Co₃O₄ for the decomposition of N₂O[J]. Acta Chim Sin, 2019, 47(4): 455–463.
- [24] NUNEZ F, CHEN L, WANG J, et al. Bifunctional Co₃O₄/ZSM-5 mesoporous catalysts for biodiesel production via esterification of unsaturated omega-9 oleic acid[J]. Catalysts, 2022, 12: 900.
- [25] PIETROGIACMI D, CAMPA M C, CARBONE L R, et al. N₂O decomposition and reduction on Co-MOR, Fe-MOR and Ni-MOR catalysts: In situ UV-vis DRS and operando FTIR investigation. An insight on the reaction pathways[J]. Appl Catal B: Environ, 2019, 240: 19–29.
- [26] GRZYBEK G, GRELUK M, PATULSKI P, et al. Adjustment of the ZSM-5 zeolite support towards the efficient hydrogen production by ethanol steam reforming on cobalt catalysts[J]. Chem Eng J, 2023, 467: 143239.
- [27] BELLMANN A, ATIA H, BENTRUP U, et al. Mechanism of the selective reduction of NO_x by methane over Co-ZSM-5[J]. Appl Catal B: Environ, 2018, 230: 184–193.
- [28] QIAO Y, GUAN Z, ZHANG M, et al. Promoting effect of Cu and Mn doping on the Fe/ZSM-5 catalyst for selective catalytic reduction of NO with NH₃[J]. Fuel, 2024, 357: 129947.
- [29] WANG Q, YANG W, DANG H, et al. Enhancement of N₂O decomposition performance by co-doping of Ni and Y to Co₃O₄ catalyst[J]. J Environ Chem Eng, 2024, 12: 112463.
- [30] LI S, ZHAO J, SONG Z, et al. New insights into the effect of polyvinyl alcohol on Co₃O₄ spinel oxide catalyst for N₂O decomposition[J]. Fuel, 2024, 362: 130745.
- [31] KANG B, GUO M, WU H, et al. Effect of alkali/alkaline-earth-metal doping on the Co₃O₄ spinel structure and N₂O decomposition[J]. Catal Sci Technol, 2024, 14: 2825–2837.
- [32] YANG W, WANG Q, DANG H, et al. In-situ polymerization intercalation of montmorillonite to achieve Co₃O₄ barrier dispersion for direct catalytic decomposition of N₂O[J]. Appl Catal A: Gen, 2023, 664: 119329.
- [33] MA Q, FU T, REN K, et al. Controllable orientation growth of ZSM-5 for methanol to hydrocarbon conversion: Cooperative effects of seed induction and medium pH control[J]. Inorg Chem, 2022, 61: 13802–13816.
- [34] OU H, YUE Y, YANG T, et al. Hydroxyl-induced electronic structure and electron transfer for improved N₂O decomposition activity of Co₃O₄[J]. ACS ES&T Eng, 2024, 5: 1032–1042.
- [35] ZHAO F, WANG D, LI X, et al. Enhancement of Cs on Co₃O₄ for N₂O catalytic decomposition: N₂O activation and O₂ desorption[J]. Ind Eng Chem Res, 2022, 61: 13854–13862.
- [36] BUTTIGNOL F, GARBUJO A, BIASI P, et al. N₂O activation and NO adsorption control the simultaneous conversion of N₂O and NO using NH₃ over Fe-ZSM-5[J]. J Am Chem Soc, 2025, 147: 8978–8990.
- [37] PIRNGRUBER G, FRUNZ L, PIETERSE J, et al. The synergy between Fe and Ru in N₂O decomposition over FeRu-FER catalysts: A mechanistic explanation[J]. J Catal, 2006, 243: 340–349.
- [38] KONDURU M, CHUANG S. Dynamics of NO and N₂O decomposition over Cu-ZSM-5 under transient reducing and oxidizing conditions[J]. J Catal, 2000, 196: 271–286.

分子筛硅铝比对活性 Co 物种微结构及催化 N₂O 分解性能的影响

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摘 要: 以 MFI 型分子筛为载体, 采用浸渍法制备了一系列不同硅铝比的 Co 基分子筛催化剂。采用 XRD、TEM、Raman、H₂-TPR、Py-FTIR 以及 XPS 等手段表征了催化剂的微观结构性质。结果表明, 催化剂表面的 Co 物种主要以钴氧化物纳米团簇和孤立 Co²⁺形式存在。其中, 孤立 Co²⁺催化 N₂O 分解活性高于钴氧化物纳米团簇。降低分子筛硅铝比有利于 Co²⁺活性位点生成, 进而提升催化活性。相较于纯硅载体的 Co/S-1, 低硅铝比的 Co/HZ60 催化 N₂O 完全分解温度可降低 80 °C, 且表现出优良的抗 O₂ 和抗 NO 性能。

关键词: 分子筛; 硅铝比; 孤立 Co²⁺; N₂O 分解

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