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Stable Nitrous Oxide Decomposition over a Beta Zeolite-Supported Cobalt Catalyst in the Presence of Oxygen

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Abstract

N₂O (Nitrous oxide) is a potent greenhouse gas with a global warming potential nearly 300 times that of CO₂ and poses a critical environmental challenge, particularly in semiconductor and display manufacturing, where it is emitted during plasma processes. However, catalytic N₂O abatement in O₂-rich environments remains inefficient because O₂ competitively occupies active sites and hinders the turnover of surface oxygen species. To clarify how support properties govern this inhibition, Co-based catalysts supported on beta zeolite, CeO₂, and TiO₂, together with unsupported Co₃O₄, were comparatively evaluated for direct N₂O decomposition. Among them, Co/Beta exhibited the highest performance, achieving >95% N₂O conversion at 450 °C in the presence of 5% O₂ with excellent long-term stability. Co/Beta possessed a high specific surface area (649 m² g⁻¹) and a mesoporous framework that favored uniform Co dispersion and reactant accessibility, while its high Co²⁺/(Co²⁺ + Co³⁺) ratio (75.5%) and large fraction of chemisorbed oxygen species (79.9%) promoted oxygen-vacancy formation and facile oxygen exchange. These results indicate that the ability of Co/Beta to maintain high activity in the presence of oxygen stems from support-modulated cobalt surface states and enhanced oxygen turnover behavior. These findings provide a support-design principle for stable N₂O decomposition under oxygen-containing exhaust conditions.

Keywords: N₂O decomposition; semiconductor and display exhaust abatement; cobalt beta zeolite; O₂-rich conditions; oxygen mobility and turnover

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1. Introduction

Fluorinated gases such as CF₄, C₂F₆, and HFCs (Hydrofluorocarbons), which have global warming potentials notably exceeding that of CO₂, have long been used for etching and chamber cleaning in the semiconductor and display industries [1–4]. These gases are directly emitted into the atmosphere or partially converted to CO₂ during plasma decomposition, thereby posing environmental concerns. To address these issues, NF₃ has been adopted as an alternative cleaning gas owing to its higher cleaning efficiency and lower direct-emission levels. Currently, semiconductor manufacturing facilities are reducing

the use of C-containing gases and expanding that of N-containing gases as alternatives [5]. However, the utilization of N-containing gases introduces another environmental challenge because N₂O is generated as a byproduct during the plasma decomposition of NF₃, which is directly emitted during plasma-enhanced chemical vapor deposition processes when incompletely consumed during oxide film deposition [6,7]. These emission mechanisms, coupled with the scale-up of industrial production, have become major contributors to the increasing release of N₂O, which is a potent greenhouse gas with a global warming potential nearly 300 times that of CO₂ and an atmospheric lifetime exceeding 100 years [8–11]. Moreover, N₂O participates in stratospheric photolysis reactions, accelerating ozone layer depletion [12–14]. Therefore, N₂O emissions from the semiconductor and display industries intensify climate change and environmental degradation and should therefore be urgently mitigated.

N₂O abatement strategies include thermal decomposition, direct catalytic decomposition, selective catalytic reduction, photocatalytic decomposition, and electrochemical reduction [12]. Conventional thermal decomposition requires high operating temperatures (>1000 °C), is energy-inefficient, and produces NO_x in process or exhaust gas streams. In contrast, direct catalytic decomposition proceeds efficiently in the intermediate temperature range of 300–600 °C, requires no additional reducing agents, and avoids the formation of secondary pollutants such as NO_x [15–17], thus holding great promise. N₂O decomposition proceeds via two primary surface reaction mechanisms, namely the Langmuir–Hinshelwood (L–H) and Eley–Rideal (E–R) pathways. In the L–H mechanism, two adsorbed O species (O*), (where * denotes a vacant active site on the catalyst surface and O* represents an oxygen atom adsorbed on such a site) recombine and desorb as O₂, whereas in the E–R mechanism, gaseous N₂O directly reacts with surface O* to produce N₂ and O₂. The reaction steps for each mechanism are as follows [18–20]:

(i) Overall reaction



(ii) L–H pathway



(iii) E–R pathway



Under O₂-rich conditions, catalytic performance is often suppressed because excess O₂ can accumulate on the surface and limit the accessibility of reactive sites for N₂O activation. Moreover, the accumulation of less reactive O species can block active sites and hinder the rate-determining step of O recombination and desorption, ultimately resulting in reduced conversion efficiency and catalyst deactivation [10,21–23]. Consequently, considerable attention has been devoted to developing high O₂-tolerance catalysts that can preserve reactive surface O species while effectively desorbing or removing inactive ones to prevent site blockage, thereby maintaining high conversion efficiency and ensuring stable N₂O decomposition in O₂-containing environments.

Accordingly, Co-based catalysts were synthesized using wet impregnation or calcination, employing various supports including beta zeolite, CeO₂, and TiO₂, as well as unsupported Co₃O₄. These catalysts were systematically evaluated to assess their resistance to activity suppression caused by competitive adsorption during N₂O decomposition un-

der O₂-rich conditions. Among them, beta zeolite is anticipated to offer distinct advantages owing to its high surface area, uniform Co dispersion, and abundant chemisorbed oxygen species, which collectively stabilize the surface cobalt oxide species with a higher Co²⁺/(Co²⁺ + Co³⁺) ratio and promote the formation of oxygen vacancies. Such features may provide favorable conditions for N₂O decomposition by facilitating the recombination and desorption of surface oxygen species involved in the L–H and E–R pathways.

2. Results and Discussion

2.1. Structural and Textural Properties

The X-ray diffraction patterns of different catalysts are presented in Figure 1a. The pattern of Co₃O₄ featured peaks at 36.8° (311), 44.8° (400), and 65.2° (440), which matched the characteristic spinel structure of Co₃O₄ [24,25]. The pattern of Co/Beta featured a sharp peak at 20.6° (302) corresponding to the beta zeolite framework [26,27]. The pattern of Co/CeO₂ showed strong peaks at 28.5° (111), 33.0° (200), and 47.4° (220) corresponding to fluorite-type CeO₂ [28,29]. The pattern of Co/TiO₂ featured peaks at 25.3° (101), 48.0° (200), and 55.1° (211) corresponding to anatase TiO₂ [30,31]. The patterns of all supported catalysts featured a weak (311) peak of spinel Co₃O₄, indicating that the Co species were partially crystallized and highly dispersed on the support because of strong metal–support interactions during impregnation and calcination [32,33]. The N₂ adsorption–desorption isotherms of all catalysts (Figure 1b) were of type IV and featured H3 hysteresis loops in the relative pressure (P/P_0) range of 0.4–0.9, indicating mesoporous structures hosting capillary condensation. Co/Beta showed the highest N₂ uptake and surface area, which suggested the formation of a well-developed mesoporous network [34,35]. Co/TiO₂ and Co/CeO₂ also exhibited mesoporous characteristics [36–38], although to a lesser extent. In contrast, Co₃O₄ displayed the lowest N₂ adsorption capacity, which indicated a poorly developed porous structure with limited textural properties [39].

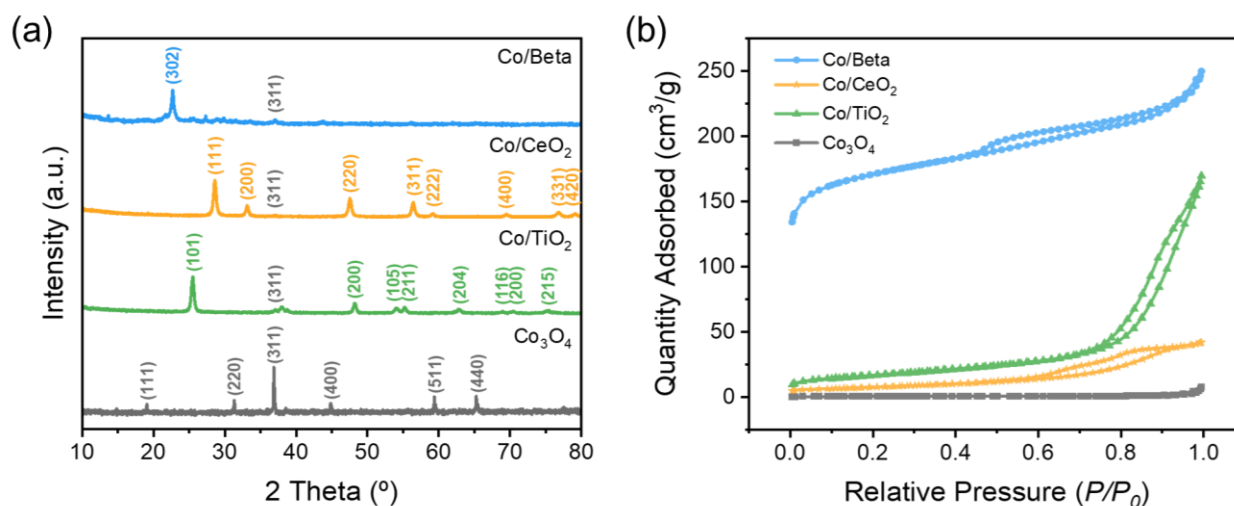


Figure 1. (a) X-ray diffraction patterns and (b) N₂ adsorption–desorption isotherms of the beta zeolite-supported Co catalyst (Co/Beta), Co/CeO₂, Co/TiO₂, and Co₃O₄.

These results demonstrate that the support material notably influenced the textural properties of the Co-based catalysts. BET analysis (Table 1) confirmed these observations. Among the catalysts, Co/Beta exhibited the most developed micro–mesoporous structure, whereas Co₃O₄ showed severely limited porosity. Co/TiO₂ and Co/CeO₂ displayed intermediate textural characteristics. Although Co/CeO₂ and Co/TiO₂ had larger average pore sizes than Co/Beta, their overall surface areas were substantially lower, indicating that the

exceptionally high surface area of Co/Beta primarily originated from a dense network of fine pores. Notably, Beta zeolite possesses a twelve-membered straight-channel framework with relatively large pore openings, which ensures uniform metal dispersion and facilitates reactant diffusion. These structural features contribute to the stabilization of the supported Co species and promote their uniform dispersion and efficient reactant diffusion within the porous channels under reaction conditions [27].

Table 1. Textural properties of Co/Beta, Co/CeO₂, Co/TiO₂, and Co₃O₄ derived from their N₂ adsorption–desorption isotherms.

Sample	BET Surface Area (m ² g ^{−1})	Pore Volume (cm ³ g ^{−1})	Pore Size (nm)
Co/Beta	649.1	0.38	2.3
Co/CeO ₂	28.4	0.06	9.1
Co/TiO ₂	60.6	0.26	17.3
Co ₃ O ₄	2.2	0.01	21.7

The spatial distribution and structural form of cobalt species were examined using TEM (Figure 2). The overall particle morphology and intrinsic microstructures of the supports were first identified from the SEM images provided in the Supporting Information (Figure S1), and high-resolution structural observations were subsequently performed using TEM.

In the Co/Beta sample (Figure 2a), the porous framework of Beta zeolite was clearly resolved, while no discrete Co₃O₄ crystallites were detected. This suggests that cobalt species exist as ultrafine (< nm-scale) CoO_x domains or partially amorphous/ionic entities located on the external surface or within the pore network [40,41]. Similar features were observed for the Co/CeO₂ and Co/TiO₂ samples (Figure 2b,c), where no well-defined crystalline Co₃O₄ nanoparticles were present and only mild contrast variations appeared across the support particles. These observations are consistent with the absence or broadening of Co₃O₄ reflections in the XRD patterns.

In contrast, the bulk Co₃O₄ sample (Figure 2d) exhibited numerous crystallites with well-defined boundaries, with particle sizes ranging widely from approximately 32 to 131 nm. The corresponding size distribution extracted from multiple TEM images is provided in the Supporting Information (Figure S2), showing an average crystallite size of 73.1 nm. These results clearly demonstrate that, unlike the supported catalysts containing ultrafine and amorphous CoO_x species, the bulk Co₃O₄ sample forms relatively large and well-crystallized Co₃O₄ particles.

HAADF–STEM–EDS mapping (Figure S3) further supports these findings: cobalt signals were broadly distributed over the support particles in the supported catalysts without any micron-scale aggregation, whereas intense Co signals were localized on individual crystallites in the bulk Co₃O₄ sample. These structural observations provide essential groundwork for interpreting the subsequent XPS-based electronic-structure analysis and comparing the catalytic performance among the samples.

2.2. Catalytic Decomposition of N₂O

N₂O decomposition performance was evaluated under two conditions, namely 5000 ppm N₂O without O₂ and with 5% O₂, with the respective N₂O conversion–temperature profiles presented in Figure 3a,b. In the absence of O₂ (Figure 3a), catalytic activity followed the order of Co/Beta (96% N₂O conversion at 450 °C) > Co₃O₄ > Co/CeO₂ > Co/TiO₂. The same trend was observed in the presence of O₂ (Figure 3b). Generally, in N₂O decomposition reactions, N₂O must be reduced on the catalyst surface to produce N₂ and O₂ [42]. However, in O₂-containing atmospheres, O₂ can accumulate on surface sites and interfere

with the adsorption or activation steps required for N_2O conversion, thereby suppressing the overall reaction rate [20]. In the presence of O_2 , the activities of Co/CeO_2 and Co_3O_4 markedly decreased, whereas Co/TiO_2 showed little change and Co/Beta maintained stable activity. For Co/Beta , the N_2O conversion achieved at 450°C in the presence of O_2 (96%) was only marginally lower than that achieved under O_2 -free conditions (96.1%), indicating a negligible activity loss (Figure 3c). In contrast, Co_3O_4 exhibited a decrease in N_2O conversion from 72.2% to 28.1% under the same conditions, corresponding to an approximately 44 percentage-point drop and indicating high sensitivity to O_2 , while Co/CeO_2 also showed a clear loss of activity. By comparison, Co/TiO_2 showed only a minor change, which is likely due to its already low intrinsic activity under O_2 -free conditions; therefore, the additional inhibitory effect of O_2 was not prominently reflected in the conversion profile [43]. During long-term stability testing (Figure 3d), Co_3O_4 showed a notable activity decrease when O_2 was introduced, although an almost complete recovery to the initial level was observed after O_2 removal. This behavior indicates that deactivation was mainly caused by the reversible accumulation of O_2 on surface sites, which temporarily limited access to reactive sites, rather than irreversible structural changes. Co/Beta maintained a consistently high N_2O conversion for >24 h regardless of O_2 presence, thus demonstrating a superior O_2 tolerance and long-term durability.

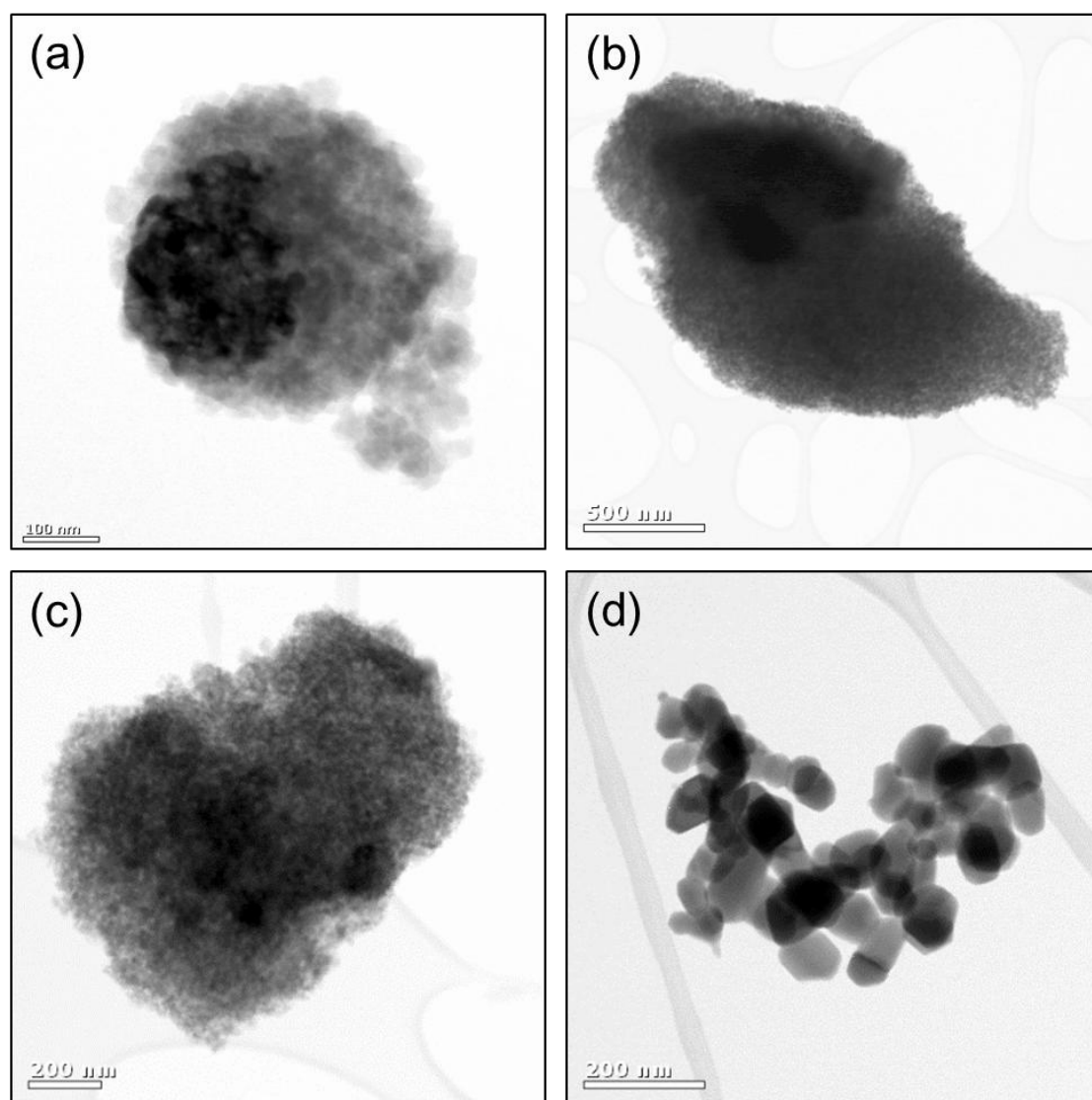


Figure 2. Transmission electron microscopy images of (a) Co/Beta , (b) Co/CeO_2 , (c) Co/TiO_2 , and (d) Co_3O_4 .

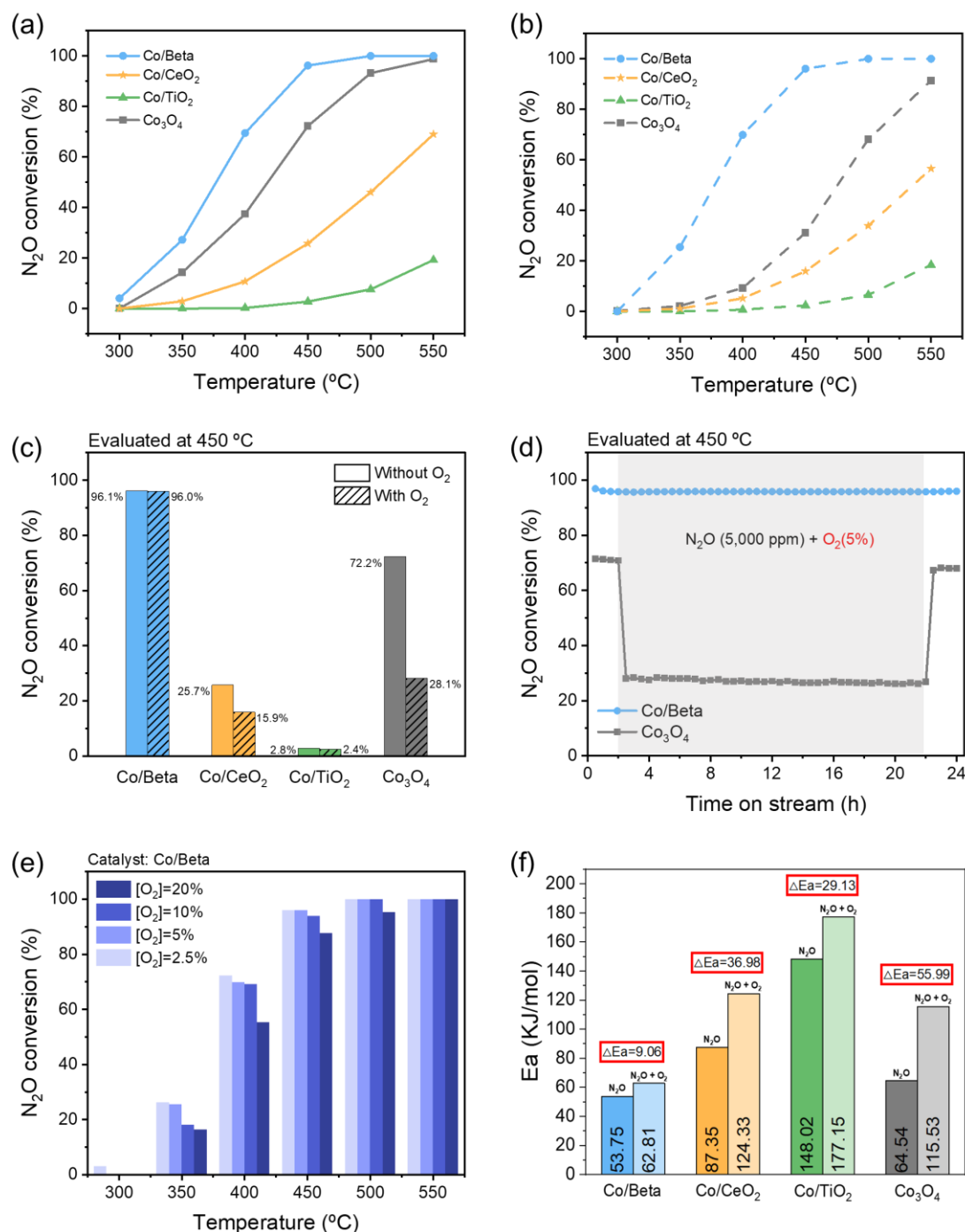


Figure 3. N₂O conversion–temperature profiles of Co-based catalysts obtained in the (a) absence and (b) presence of O₂. (c) N₂O conversion achieved by catalysts at 450 °C in the presence and absence of O₂. (d) Results of long-term stability testing under alternating O₂ on/off conditions. The grey shaded region indicates the period in which O₂ was present. (e) N₂O conversion as a function of O₂ concentration for Co/Beta. (f) Apparent activation energies (E_a) for N₂O decomposition over all catalysts under N₂O-only and N₂O + O₂ (5%) Reaction conditions: 5000 ppm N₂O, 5% O₂ (when used) balanced by N₂, total flow rate of 500 cc min^{−1}, GHSV of 60,000 h^{−1}.

To elucidate the material-dependent O₂ tolerance more clearly, additional N₂O decomposition experiments were conducted by varying the O₂ concentration from 2.5 to 20% (Figure 3e). Co/Beta maintained nearly identical N₂O conversion across the entire O₂

range, and the activity loss at 450 °C remained negligible even under 20% O₂. Such behavior suggests that O₂ does not significantly hinder access to the active Co species on Co/Beta and that the accumulation of strongly bound, inactive oxygen species is effectively suppressed. Consequently, Co/Beta exhibits stable N₂O decomposition performance regardless of external O₂ partial pressure.

In contrast, Co₃O₄ displayed a pronounced decrease in N₂O conversion as the O₂ concentration increased over the whole temperature range (Figure S4). This O₂-induced inhibition can be interpreted in the context of the mechanistic behaviors reported for metal oxides. N₂O decomposition may proceed through both Langmuir–Hinshelwood (L–H) and Eley–Rideal (E–R) routes, and oxygen inhibition has been observed for both pathways. Excess O₂ can accumulate on the surface and limit the accessibility or turnover of reactive oxygen species—often described as competitive adsorption behavior—which hinders the regeneration or utilization of O*. In addition, high O₂ concentrations may oversaturate the surface or shift the oxidation state of Co centers (Co²⁺ → Co³⁺), thereby suppressing the N₂O activation step associated with the E–R pathway as well [44].

Therefore, the contrasting O₂ responses of Co/Beta and Co₃O₄ indicate that the Co species in Co/Beta are inherently less susceptible to O₂-induced site blocking and surface oxygen oversaturation due to their framework-stabilized structural and surface characteristics. To further clarify these mechanistic differences, additional characterization analyses were performed.

Figure 3f compares the apparent activation energies (E_a) obtained from the Arrhenius plots for N₂O decomposition, with the full temperature-dependent Arrhenius plots provided in the Supporting Information (Figure S5). Under N₂O-only conditions (5000 ppm N₂O, 5% O₂ when used, N₂ balance, GHSV = 500,000 h^{−1}), Co/Beta exhibited the lowest E_a value, suggesting relatively facile activation of the N–O bond. In contrast, Co/CeO₂, Co/TiO₂, and Co₃O₄ displayed higher E_a values, indicating limited formation of reactive O* species in the low-temperature region [18,45].

When 5% O₂ was introduced, the apparent activation energies for N₂O decomposition over Co/CeO₂, Co/TiO₂, and Co₃O₄ increased noticeably, indicating that the reaction required a higher energy barrier in the presence of oxygen. This behavior can be attributed to O₂-induced inhibition, including competitive adsorption and the accumulation of less-reactive oxygen species on the catalyst surface, which hinder active-site regeneration. In contrast, Co/Beta showed only a small change in apparent activation energy upon O₂ addition. This result indicates that the apparent activation energy for N₂O decomposition over Co/Beta changed only slightly in the presence of O₂, suggesting that the reaction energy barrier was minimally influenced by oxygen. The Arrhenius plots in the Supporting Information (Figure S5) further support this interpretation, as Co/Beta exhibits very similar slopes under N₂O-only and N₂O + O₂ conditions, indicating only a minor kinetic penalty in the presence of oxygen.

2.3. Surface Chemical States, Redox and Adsorption Properties

The X-ray photoelectron spectra of all catalysts featured Co 2p (Figure 4a) and O 1s (Figure 4b) signals. All Co 2p spectra featured Co²⁺ and Co³⁺ peaks. For Co/CeO₂, the Co 2p region partially overlapped with the Ce MNN Auger peak; however, deconvolution enabled a clear distinction of the Co²⁺ and Co³⁺ contributions [46]. The binding energies of the Co 2p peaks were reported to vary within ±0.5 eV depending on the catalyst type, which was attributed to differences in the electronic environment and metal–support interaction—a phenomenon commonly observed for supported Co oxide catalysts. For Co/Beta, the Co²⁺ peaks were observed at 781.9 eV (2p_{3/2}) and 797.9 eV (2p_{1/2}), while the

Co³⁺ peaks appeared at 779.9 eV (2p_{3/2}) and 795.2 eV (2p_{1/2}) [47–49]. The simultaneous presence of both Co²⁺ and Co³⁺ indicated the formation of a mixed-valence Co oxide phase with a spinel-type structure on the beta zeolite support.

Based on the deconvolution results, the Co²⁺/(Co²⁺ + Co³⁺) ratios followed the order of Co/Beta (75.5%) > Co/CeO₂ (53.2%) > Co₃O₄ (49.5%) > Co/TiO₂ (37.7%). As Co²⁺ is recognized as the primary active site responsible for cleaving the N–O bond in N₂O, a higher Co²⁺/(Co²⁺ + Co³⁺) ratio is beneficial for enhancing catalytic activity [29]. Therefore, the superior catalytic performance of Co/Beta can be directly ascribed to its high Co²⁺/(Co²⁺ + Co³⁺) ratio, with the redox behavior of surface cobalt oxide species having a higher Co²⁺/(Co²⁺ + Co³⁺) ratio playing a critical role in the N₂O decomposition mechanism. In particular, electron exchange between Co²⁺ and Co³⁺ facilitates the formation of oxygen vacancies. The surface cobalt oxide species having a higher Co²⁺/(Co²⁺ + Co³⁺) ratio is also indicative of the degree of surface defects and shows a positive correlation with the presence of oxygen vacancies. These vacancies further promote catalytic activity by enhancing oxygen mobility and active site availability [19,50].

The O 1s spectra provided further insights into the surface oxygen species. Co/Beta exhibited a remarkably high proportion of O_{chem}, accounting for 79.9% of the total surface oxygen. This high O_{chem} content suggests that the Co/Beta surface may contain abundant oxygen vacancies [51,52], which are generally associated with enhanced oxygen mobility and easier desorption. The presence of abundant O_{chem} is also likely to facilitate the reduction of Co³⁺ to Co²⁺, thereby contributing to the increased Co²⁺/(Co²⁺ + Co³⁺) ratio. In comparison, the O_{chem} contents of Co₃O₄, Co/TiO₂, and Co/CeO₂ were 47.6%, 43.1%, and 39.6%, respectively [53,54]. These lower O_{chem} values correlate with the reduced Co²⁺/(Co²⁺ + Co³⁺) ratios and the lower densities of reactive oxygen species observed for these catalysts, which are probably related to differences in their electronic structures and metal–support interactions.

Co-based catalysts are generally deactivated under O₂-rich conditions because of the competitive adsorption of N₂O and O₂ on the same active sites [10,21,55]. However, Co/Beta maintained stable performance even in the presence of O₂. This finding can be explained by the results of XPS analysis, which show that the beta zeolite not only stabilized the surface Co species with a higher Co²⁺/(Co²⁺ + Co³⁺) ratio but also promoted the formation of a surface structure with an exceptionally high content of O_{chem}. Such characteristics are likely to accelerate the turnover and low-temperature desorption of surface oxygen species during O₂ adsorption–desorption, thereby alleviating site blocking and mitigating the inhibitory effect of O₂. Moreover, the three-dimensional channel system of beta zeolite promotes the uniform dispersion of Co species and efficient mass transport, which help maintain active-site accessibility and suppress O₂-induced site blockage under O₂-rich conditions.

Co/Beta exhibited the highest Co²⁺/(Co²⁺ + Co³⁺) ratio (75.5%) and O_{chem} (79.9%) fractions among the tested catalysts (Table 2), which highlighted its excellent surface redox properties essential for achieving high catalytic activity and O₂ tolerance. The structural and electronic advantages provided by the beta zeolite promoted the stabilization of surface cobalt oxide species with a higher Co²⁺/(Co²⁺ + Co³⁺) ratio, while the enhanced Co³⁺ ↔ Co²⁺ redox cycling facilitated the formation of oxygen vacancies, which in turn contributed to improved O₂ mobility and greater exposure of active sites [56], thereby enabling efficient N₂O decomposition even under O₂-rich conditions. This interpretation is further supported by the H₂-TPR, O₂-TPD, and N₂O-TPD results, which revealed facile Co³⁺ → Co²⁺ reduction, abundant low-temperature oxygen desorption, and enhanced N₂O activation.

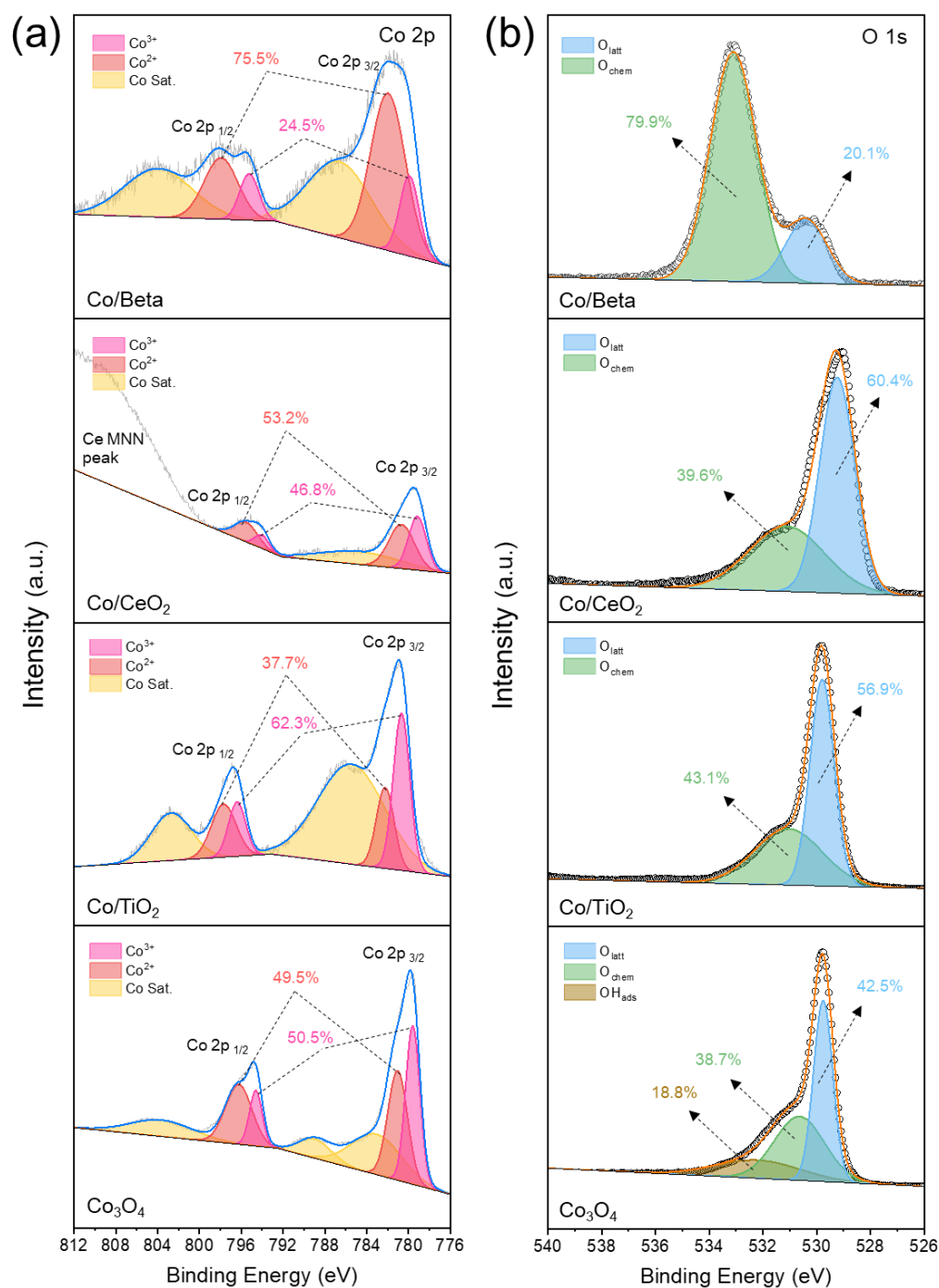


Figure 4. X-ray photoelectron spectroscopy spectra of (a) Co 2p and (b) O 1s spectra for Co/Beta, Co/CeO₂, Co/TiO₂, and Co₃O₄. The blue line in the Co 2p spectra and the orange line in the O 1s spectra represent the overall fitted envelopes.

Table 2. Relative surface ratios of Co²⁺/(Co²⁺ + Co³⁺) and O_{chem}/(O_{chem} + O_{latt}) determined by means of X-ray photoelectron spectroscopy.

Sample	Co ²⁺ /(Co ²⁺ + Co ³⁺) (%)	O _{chem} /(O _{chem} + O _{latt}) (%)
Co/Beta	75.5	79.9
Co/CeO ₂	53.2	39.6
Co/TiO ₂	37.7	43.1
Co ₃ O ₄	49.5	47.6

Catalyst reducibility was evaluated by H₂-TPR (Figure 5a). Co/Beta exhibited two well-defined reduction peaks at 280 and 307 °C, attributable to the reduction of surface Co³⁺ species in Co₃O₄ to Co²⁺ and bulk reduction of Co₃O₄ to CoO [32]. These low-temperature reduction features indicated that Co species were highly dispersed within the beta zeolite framework and that excessive metal–support interactions were effectively mitigated, which facilitated reduction. Notably, the 12-membered straight-channel structure of beta zeolite provided sufficient spatial capacity for Co dispersion and enabled the uniform anchoring of metal ions, which enhanced the reducibility and accessibility of active sites. Co/CeO₂ displayed two reduction peaks at 295 and 350 °C [57], attributable to the stepwise reduction of Co₃O₄ to CoO and Co⁰, respectively. This low-temperature reduction behavior was probably promoted by the O storage capacity of CeO₂ and its ability to facilitate lattice O mobility [58]. For unsupported Co₃O₄, two peaks at 340 and 420 °C were observed [59,60], corresponding to the conventional stepwise reduction of Co₃O₄ to CoO and Co⁰, respectively. For Co/TiO₂, two higher-temperature peaks at 394 and 425 °C were observed [61], suggesting delayed reducibility due to the strong anchoring of Co species on the TiO₂ surface or their poor dispersion. These reduction features were strongly support-dependent, with Co/Beta showing the most favorable low-temperature reducibility. Overall, Co/Beta exhibited the lowest reduction temperatures, indicating that the Co³⁺ → Co²⁺ transition occurred most readily under the applied conditions [62]. This observation was consistent with the XPS results, which showed that Co/Beta possessed the highest Co²⁺/(Co²⁺ + Co³⁺) ratio (75.5%). The concordance between the XPS and H₂-TPR results indicates that the beta zeolite facilitated the formation and stabilization of catalytically active Co²⁺ species, thereby contributing to the enhanced intrinsic activity for N₂O decomposition.

The O₂ desorption characteristics of the catalysts were investigated via O₂-TPD (Figure 5b). Under O₂-rich conditions, molecular O₂ can compete with N₂O for accessible surface sites and can also increase the surface oxygen coverage, both of which may inhibit N₂O decomposition [45,63]. Therefore, probing the adsorption–desorption behavior of oxygen is important for assessing the O₂ tolerance of catalysts. In many N₂O decomposition systems, the overall rate is strongly influenced by the removal of surface oxygen species (O*) formed during N–O bond scission, because slow O* recombination/desorption hampers active-site regeneration [64]. Accordingly, a catalyst that can efficiently turnover and desorb adsorbed oxygen is expected to show improved stability in O₂-containing feeds.

Figure 5b illustrates these differences in O₂ desorption behavior among the catalysts. O₂-TPD profiles provide information on the amount, desorption temperature, and reactivity of surface and lattice O. In particular, the low-temperature region (60–240 °C) is mainly associated with desorption of highly reactive surface O species such as O²⁻ (superoxide) or O⁻ (chemisorbed atomic O), which are generally regarded as active O species that can directly participate in N₂O decomposition. In contrast, temperatures of above 240 °C correspond to the gradual desorption of lattice O, which is relatively unreactive and contributes to the reaction only at elevated temperatures [29].

As shown in Figure 5b, the O₂-TPD profiles reveal clear differences in oxygen desorption behavior among Co/Beta, Co/CeO₂, Co/TiO₂, and Co₃O₄. Following the common assignment, the low-temperature region (60–240 °C) is mainly associated with the release of weakly bound, labile surface oxygen species (e.g., defect- or vacancy-associated oxygen), whereas the higher-temperature region (>240 °C) reflects the gradual desorption of more strongly bound oxygen, often linked to lattice/subsurface oxygen and oxygen migration processes [65,66]. Notably, Co/Beta exhibits the largest low-temperature desorption feature, indicating a higher abundance of readily removable surface oxygen species and a

greater oxygen turnover capability compared with the oxide-supported catalysts. In contrast, Co_3O_4 shows the weakest desorption signal over the entire temperature range, suggesting limited oxygen lability and a less efficient regeneration of oxygen-covered sites. Co/TiO_2 and Co/CeO_2 display intermediate behavior, with Co/TiO_2 exhibiting a more pronounced low-temperature feature than Co/CeO_2 . Overall, these trends suggest that the greater oxygen lability/turnover of Co/Beta under O_2 -rich feeds may mitigate O_2 -induced inhibition by promoting active-site regeneration and preserving access to reactive sites.

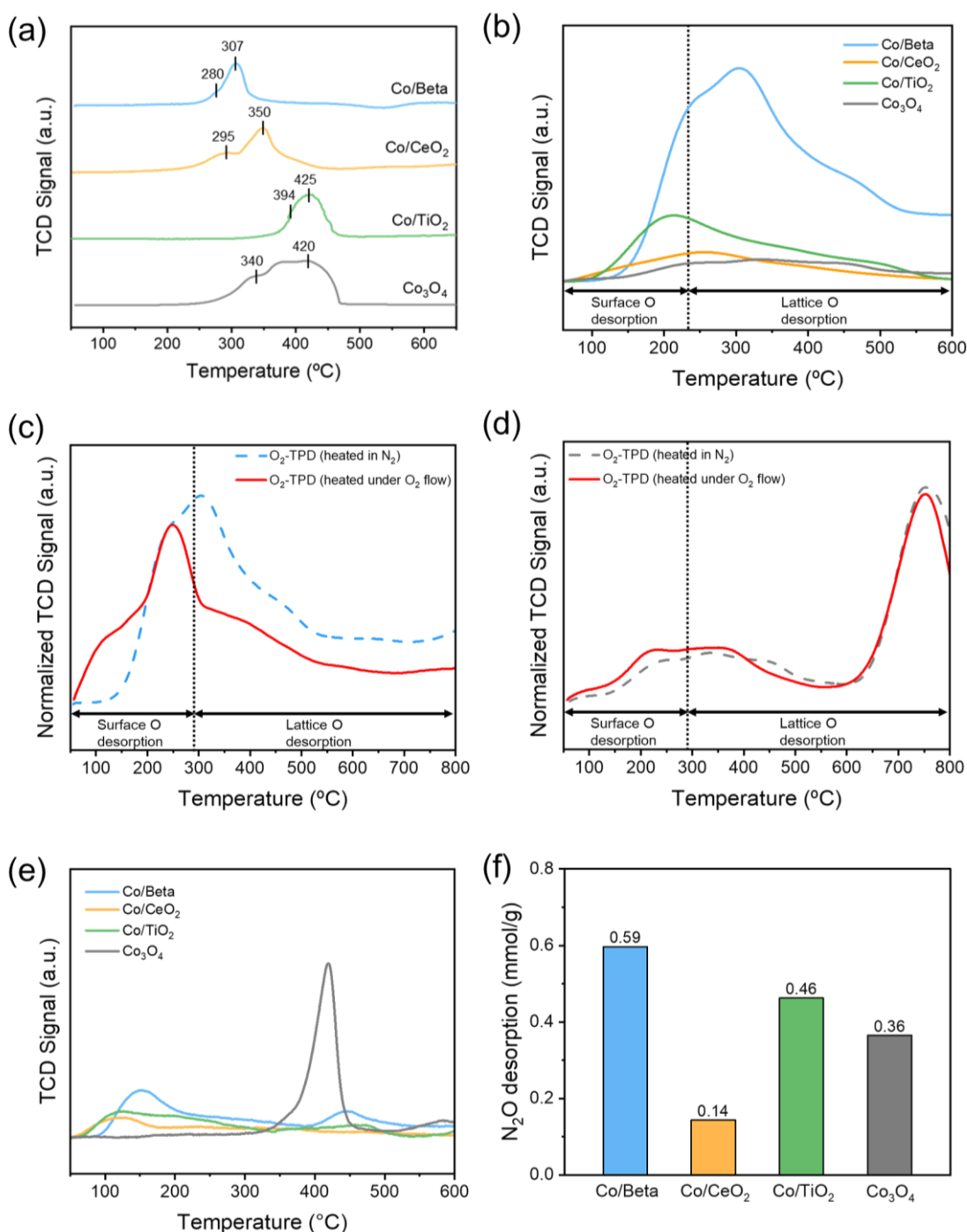


Figure 5. (a) H_2 temperature-programmed reduction profiles of Co/Beta , Co/CeO_2 , Co/TiO_2 , and Co_3O_4 . (b) O_2 temperature-programmed desorption profiles of the catalysts. (c,d) O_2 -TPD profiles of Co/Beta (c) and Co_3O_4 (d) recorded after O_2 pre-adsorption under different heating atmospheres (heated in N_2 vs. under continuous O_2 flow). The vertical dashed line separates the surface oxygen

and lattice oxygen desorption regions. (e) N₂O temperature-programmed desorption profiles and (f) comparison of N₂O desorption amounts.

To further probe oxygen desorption under O₂-rich environments, O₂-TPD profiles were collected after O₂ pre-adsorption while heating either in inert N₂ or under a continuous O₂ flow (Figure 5c,d). Unlike conventional TPD in N₂, heating under O₂ flow enables concurrent desorption and re-adsorption/oxygen exchange, thereby providing a qualitative descriptor of dynamic oxygen turnover relevant to N₂O decomposition in the presence of O₂. For Co/Beta, the profile recorded under O₂ flow shows a pronounced shift of the low-temperature desorption feature to lower temperatures compared with the N₂-heated trace (Figure 5c), demonstrating that surface oxygen species are more readily removed and turned over under O₂-containing feeds. This facilitated oxygen turnover is expected to accelerate active-site regeneration and mitigate O₂-induced inhibition by preventing excessive oxygen coverage and maintaining access to reactive sites [45,67]. In contrast, Co₃O₄ exhibits only minor changes in the low-temperature region and retains a prominent high-temperature desorption feature under O₂ flow (Figure 5d), indicating more strongly stabilized oxygen species and less efficient regeneration of oxygen-covered sites in O₂-rich environments. Overall, these atmosphere-dependent O₂-TPD behaviors support a higher oxygen turnover capability for Co/Beta under O₂, consistent with its improved robustness during O₂-containing N₂O decomposition.

The results of N₂O-TPD measurements are presented in Figure 5e,f. Co₃O₄ exhibited a sharp and intense single high-temperature peak centered at ~420 °C, which indicates a lack of low-temperature active oxygen species and suggests that N₂O activation primarily occurred through lattice O at elevated temperatures (Figure 5e). Compared with the other catalysts, Co/Beta displayed a markedly stronger low-temperature peak at ~200 °C, which implied the presence of abundant reactive O species such as O²⁻ or O⁻ that facilitated N₂O dissociation and O₂ release at lower temperatures [55,68]. Co/CeO₂ and Co/TiO₂ exhibited broad and weak desorption features across the entire temperature range, which suggested a heterogeneous distribution of active sites with low intrinsic activity.

Figure 5f compares different catalysts in terms of their N₂O desorption amounts. Co/Beta exhibited the highest desorption amount, which confirmed its superior ability to supply active O species at low temperatures and agreed with the results of O₂-TPD measurements (Figure 5b). The O₂-TPD curve of Co/Beta showed a strong low-temperature desorption peak below 200 °C, indicating the facile release of surface-active O species and high O mobility. Therefore, the abundance of low-temperature O species and their facile desorption, as evidenced by O₂-TPD and N₂O-TPD results, represent key factors governing the O₂ tolerance and sustained N₂O decomposition activity of catalysts.

Figure 6 shows the in situ DRIFTS spectra of Co/Beta and Co₃O₄ recorded under a continuous flow of 1000 ppm N₂O + 5% O₂ in N₂ (500 sccm), used to elucidate the nature of surface species formed under reaction-relevant conditions. To directly monitor the temperature-dependent evolution of adsorbates during N₂O decomposition in the presence of oxygen, spectra were first collected during an adsorption stage at 50 °C for 15 min (Figure 6a,b), followed by temperature-programmed measurements under the same continuous-flow condition while increasing the temperature from 100 to 450 °C (Figure 6c,d).

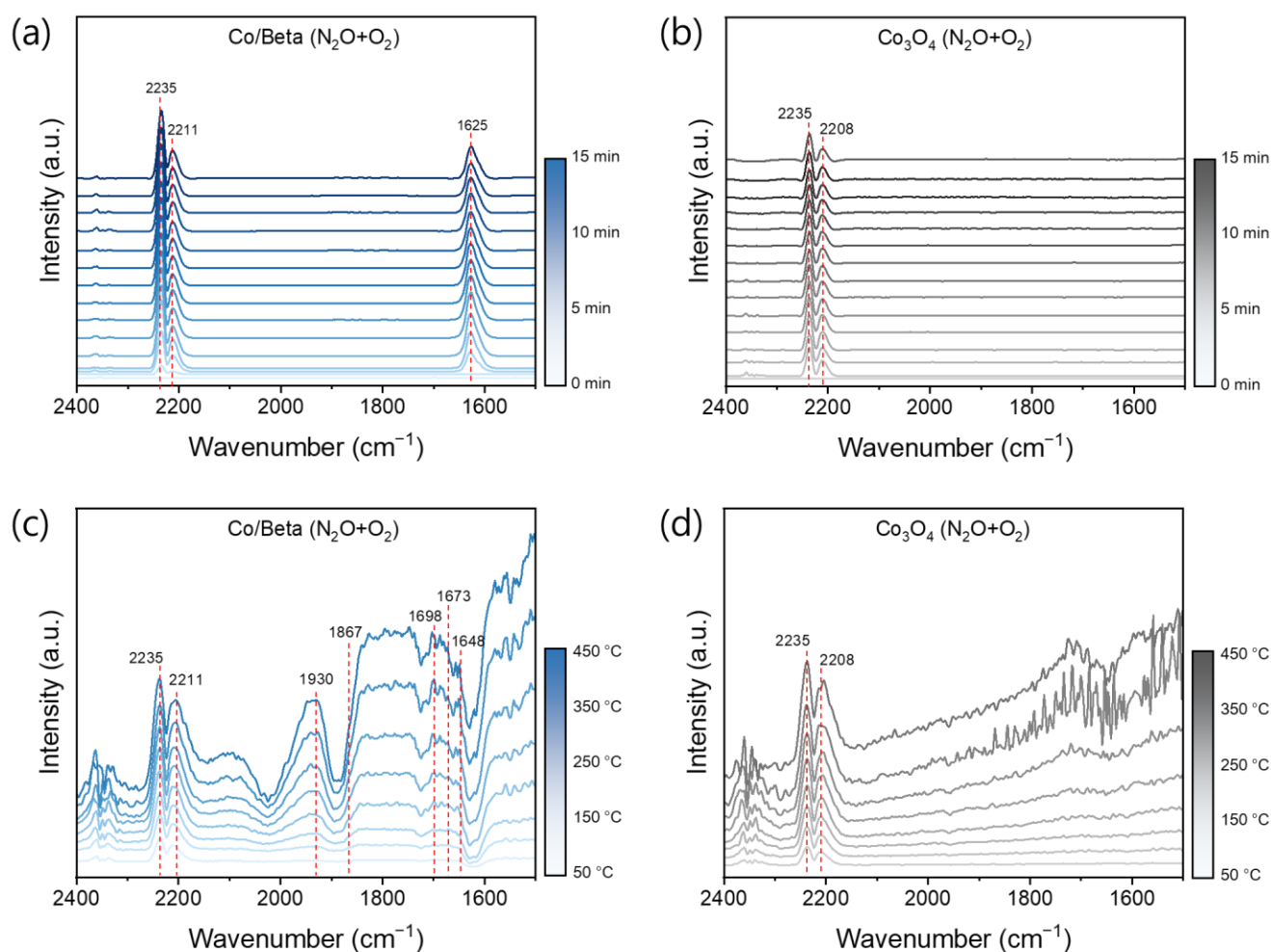


Figure 6. In situ diffuse reflectance infrared Fourier transform spectra of Co/Beta and Co_3O_4 under 1000 ppm N_2O + 5% O_2 in N_2 (500 sccm): adsorption at 50 °C (a,b) and temperature-programmed measurement under continuous flow (c,d), temperature-dependent evolution of surface species.

The characteristic spectral signatures of adsorbed N_2O were observed as paired bands in the 2240–2200 cm^{-1} region, assigned to N–N stretching. These paired features are widely recognized as fingerprint signals of weakly bound N_2O on oxide- and Co-based catalysts [69]. In addition, NO_x -related surface species were monitored mainly in the 1950–1500 cm^{-1} region. A band near ~ 1930 cm^{-1} is consistent with nitrosyl-/NO-derived adsorbates on cobalt sites [70], whereas a feature around 1867 cm^{-1} is commonly assigned to adsorbed NO on metal cation sites [71]. Bands in the 1700–1650 cm^{-1} region are commonly assigned to nitrate/nitrite-type surface species, and features near ~ 1624 – 1625 cm^{-1} can likewise be attributed to nitrate/nitrite-related adsorbates [72,73]. However, nitrate/nitrite-related bands can be weak or even absent during temperature-programmed measurements because these species are thermally labile and decompose rapidly at elevated temperatures [71]. Therefore, the absence of distinct bands in these regions should be interpreted as limited steady-state accumulation rather than conclusive evidence for the complete suppression of transient NO_x formation [73].

In the adsorption step at 50 °C (Figure 6a,b) under a continuous flow of N_2O + O_2 , both Co/Beta and Co_3O_4 exhibit the characteristic paired bands in the 2240–2200 cm^{-1} region (2235/2211 cm^{-1} for Co/Beta and 2235/2208 cm^{-1} for Co_3O_4), indicating that N_2O is readily adsorbed on both catalysts at low temperature. A clear difference, however, is that

nitrate/nitrite-related features below 1700 cm^{-1} are discernible for Co/Beta, whereas no comparable features are clearly resolved on Co_3O_4 within the same adsorption period.

This selective appearance on Co/Beta can be attributed to the distinct surface environment created by the Beta zeolite support. The Brønsted/Lewis acidity and microporous confinement of Beta can promote the transient formation and detection of nitrate/nitrite-type species at low temperature [74,75]. Importantly, such species are often thermally labile and therefore are not necessarily expected to persist as strongly accumulated, site-blocking adsorbates under the subsequent high-temperature reaction regime. In addition, Co/Beta likely provides a higher density of well-dispersed cobalt sites than bulk Co_3O_4 , consistent with the XPS results (Figure 4 and Table 2). This interpretation is further supported by the XRD pattern (Figure 2a), where the Co_3O_4 reflections for Co/Beta are very weak, suggesting that cobalt oxide domains are highly dispersed and/or present as small crystallites. Specifically, Co/Beta shows a markedly higher surface Co^{2+} fraction ($\text{Co}^{2+}/(\text{Co}^{2+} + \text{Co}^{3+}) = 75.5\%$) than Co_3O_4 (49.5%), together with a notably elevated O_{chem} ratio ($\text{O}_{\text{chem}}/(\text{O}_{\text{chem}} + \text{O}_{\text{latt}}) = 79.9\%$ for Co/Beta, compared with 47.6% for Co_3O_4). The coexistence of Co^{2+} -enriched sites and abundant labile surface oxygen species suggests more facile surface redox chemistry and oxygen exchange on Co/Beta under $\text{N}_2\text{O} + \text{O}_2$, which can mitigate O_2 -induced inhibition during N_2O decomposition. By contrast, on Co_3O_4 , nitrate/nitrite-type species may either form only to a limited extent or be rapidly transformed/decomposed without leaving detectable signatures over the same timescale.

During the subsequent temperature-programmed measurements under continuous $\text{N}_2\text{O} + \text{O}_2$ flow (Figure 6c,d), the evolution of surface species differs markedly between Co/Beta and Co_3O_4 . For Co/Beta (Figure 6c), the N_2O twin bands at 2235 and 2211 cm^{-1} progressively decrease with increasing temperature, while new bands develop in the $1950\text{--}1500\text{ cm}^{-1}$ region. In particular, features near ~ 1930 and $\sim 1867\text{ cm}^{-1}$ emerge, which are consistent with nitrosyl-/NO-derived adsorbates on cobalt sites and adsorbed NO on metal cation sites, respectively. Additional bands also appear in the $1700\text{--}1600\text{ cm}^{-1}$ region (e.g., ~ 1698 , 1673 , and 1648 cm^{-1}), suggesting the formation and evolution of nitrate/nitrite-type surface species under the reaction stream. Importantly, these NO_x -related features are better interpreted as dynamically evolving intermediates rather than as stably accumulated, site-blocking poisons, as evidenced by their pronounced temperature-dependent formation and transformation. This behavior suggests that adsorbed N_2O is transformed into reactive surface intermediates during heating and that surface turnover remains active on Co/Beta under O_2 -containing conditions. Consistent with the XPS/ O_2 TPD indications of abundant labile oxygen and facile oxygen exchange, such dynamic intermediate evolution suggests a more efficient turnover of oxygen-covered sites, thereby maintaining access to reactive sites even at elevated temperatures [45].

In contrast, Co_3O_4 (Figure 6d) exhibits a comparatively limited development of NO_x -related bands over the same temperature range. The N_2O twin bands at 2235 and 2208 cm^{-1} persist to higher temperatures with only moderate attenuation, and a broad feature around $\sim 1718\text{ cm}^{-1}$ becomes discernible at elevated temperatures, whereas distinct nitrosyl/NO bands in the $1900\text{--}1800\text{ cm}^{-1}$ region are not clearly resolved. This behavior suggests that, under O_2 -rich flow, the Co_3O_4 surface may experience stronger competitive oxygen occupation of accessible sites, which can restrict N_2O activation and limit the detectable accumulation of NO_x -type intermediates [63]. Overall, the temperature-programmed DRIFTS profiles indicate that Co/Beta sustains a more dynamic surface redox chemistry—characterized by the formation and transformation of reactive intermediates—whereas Co_3O_4 shows comparatively muted intermediate evolution, consistent with stronger O_2 -induced inhibition.

2.4. Effects of Coexisting Gases on Catalytic Performance

N₂O decomposition rarely occurs in single-gas environments, as O₂, NO, and H₂O commonly coexist and can significantly affect catalytic behavior. O₂ and NO compete with N₂O for the same active sites on the catalyst surface, whereas H₂O tends to form hydroxyl species blocking or deactivating these sites [76–80]. Consequently, catalytic activity and stability can be notably suppressed depending on the type and concentration of coexisting gases, and evaluating the influence of O₂, NO, and H₂O is essential for understanding catalyst behavior under realistic operating conditions.

Figure 7a–d compare the N₂O decomposition performances of Co/Beta, Co/CeO₂, Co/TiO₂, and Co₃O₄ under various coexisting-gas conditions. Although the presence of O₂ and NO inhibited all catalysts, the inhibition extent depended on the support. Co/Beta exhibited the highest activity, which is primarily attributed to its abundant low-temperature active oxygen species and favorable surface redox properties. The high surface area and mesoporous framework of beta zeolite contributed to improving the uniform dispersion of Co species and reactant accessibility, thereby supporting the overall catalytic performance, although they do not serve as direct determining factors. In addition, XPS and O₂/N₂O-TPD analyses revealed that Co/Beta possessed the highest Co²⁺/(Co²⁺ + Co³⁺) ratio (75.5%) and O_{chem} (79.9%) fractions, both of which promoted O vacancy formation and enhanced O mobility, thereby accounting for the outstanding O₂ tolerance. Indeed, Co/Beta achieved nearly complete N₂O conversion above 450 °C and maintained remarkable resistance to O₂ and NO. In contrast, Co/CeO₂ and Co₃O₄ suffered from severe activity loss due to competitive adsorption, with Co₃O₄ showing 72% conversion at 450 °C but >40% inhibition when coexisting gases were introduced. Co/TiO₂ displayed intrinsically poor performance with negligible improvement or inhibition under O₂ and NO. This behavior was attributed to low surface area, which restricted Co dispersion, and limited O mobility, which hindered the supply of reactive O species. Additionally, under conditions where O₂, NO, and H₂O coexisted, all catalysts exhibited pronounced activity suppression, with H₂O exacerbating the inhibitory effect (Figure S6). These results demonstrate that water acts as a critical poisoning species under realistic flue gas compositions.

Figure 7e shows the time-dependent behavior of Co/Beta and Co₃O₄ during the sequential introduction and removal of coexisting gases (500 ppm N₂O, 5% O₂, 500 ppm NO, and 5% H₂O, N₂ balance, GHSV = 60,000 h^{−1}). For Co/Beta, the N₂O conversion was 96% at 450 °C under N₂O alone and decreased by <1% when O₂ and NO were introduced sequentially, indicating remarkable stability. By contrast, Co₃O₄ exhibited an initial conversion of 72% for N₂O alone, which dropped sharply to 28% upon the co-feeding of O₂ and NO. The introduction of H₂O caused a dramatic decline, reducing N₂O conversion over Co/Beta and Co₃O₄ to 25% and 13%, respectively. Upon the sequential removal of coexisting gases, Co/Beta rapidly recovered to >96% conversion immediately after H₂O was cut off and fully restored its initial activity once NO and O₂ were subsequently removed. In contrast, Co₃O₄ showed only minimal recovery from 13% to 23% after H₂O removal, and its conversion stabilized at 51% after all coexisting gases had been eliminated, which corresponded to an irreversible initial activity loss of 21%. These results suggest that the superior performance of Co/Beta was due to its high Co²⁺/(Co²⁺ + Co³⁺) ratio and abundant O_{chem}, which helped stabilize the surface active sites and sustain activity in the presence of impurities, whereas Co₃O₄ suffered from irreversible poisoning due to the formation of hydroxyl species under H₂O-rich conditions.

Co₃O₄ suffered from substantial irreversible deactivation in the presence of H₂O, which resulted in poor long-term stability. In contrast, Co/Beta showed negligible inhibition under O₂ and NO, exhibited the complete recovery of its initial activity after coexisting-gas removal, and maintained high N₂O conversion (96%) even at 550 °C in the presence of O₂, NO, and H₂O. Therefore, although both catalysts were vulnerable to water

vapor, Co/Beta demonstrated excellent reversibility and high-temperature stability, thus holding promise for practical applications in N₂O abatement under coexisting-gas conditions.

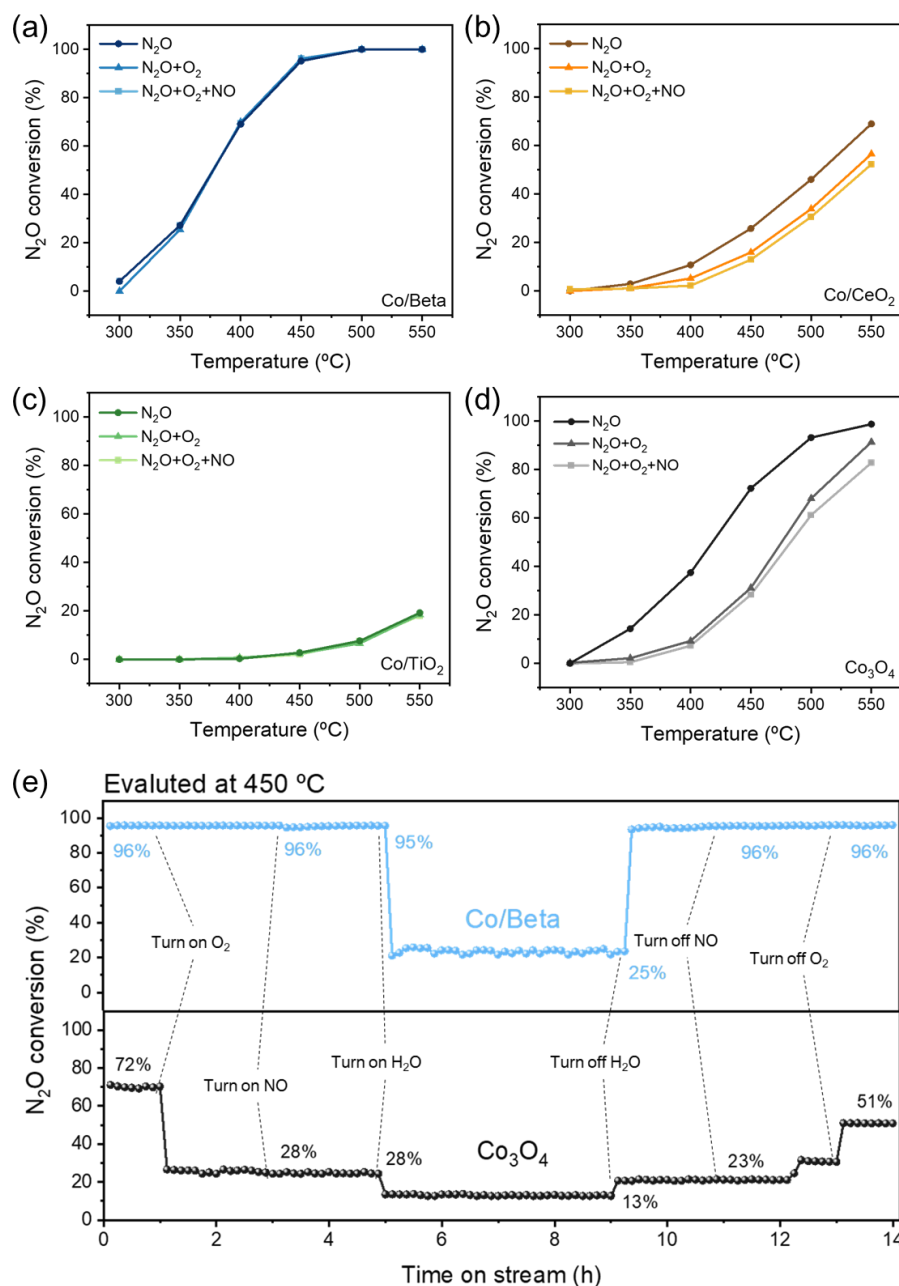


Figure 7. N₂O decomposition performances of (a) Co/Beta, (b) Co/CeO₂, (c) Co/TiO₂, and (d) Co₃O₄ under various conditions, namely 500 ppm N₂O, 5% O₂ (when used), 500 ppm NO (when used), N₂ balance, GHSV = 60,000 h^{−1}. (e) Time-on-stream-dependent N₂O conversion over Co/Beta and Co₃O₄ at 450 °C with the sequential introduction and removal of O₂, NO, and H₂O (5% O₂, 500 ppm NO, and 5% H₂O when used).

3. Materials and Methods

3.1. Materials

Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, CAS 10026-22-9, product no. 230375, reagent grade, 98%) and Ammonium-form beta zeolite (Al₂O₅Si, CAS 1318-02-1, product no. 045874) were purchased from Thermo Fisher Scientific (Waltham, MA, USA). Cerium

oxide (CeO_2 , CAS 1306-38-3, product no. 202975, powder, 99.995% trace metals basis) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Titanium(IV) oxide (anatase, TiO_2 , CAS 1317-70-0, catalog no. 8613-1405, assay 98%, CP grade) was purchased from Daejung Chemicals & Metals Co., Ltd. (Siheung, Republic of Korea).

3.2. Catalytic Synthesis

The catalysts were synthesized using a wet impregnation method. Co was introduced in the form of cobalt (II) nitrate hexa-hydrate. Ammonium-form beta zeolite, cerium (IV) oxide, and titanium dioxide were used as supports. An appropriate amount of cobalt (II) nitrate hexa-hydrate was dissolved in deionized water to prepare a 5 wt% Co solution. The solution was supplemented with the desired support, stirred at 80 °C for 6 h using a magnetic hot plate, and then heated at 60 °C overnight in an oil bath to evaporate the solvent. The obtained powder was calcined in air at 550 °C for 6 h at a heating rate of 5 °C min⁻¹ to afford a catalyst with a Co loading of 5 wt%. Additionally, cobalt (II) nitrate hexa-hydrate was calcined under the abovementioned conditions to obtain Co_3O_4 . Hereafter, these catalysts were denoted as Co/Beta, Co/ CeO_2 , Co/ TiO_2 , and Co_3O_4 , respectively.

3.3. Catalytic Characterization

Structural characteristics were probed by X-ray diffraction (D8 Advance, Bruker, Billerica, MA, USA) using $\text{Cu K}\alpha$ radiation over a 2θ range of 10–80°. Specific surface areas and pore volumes were determined by BET and Barrett–Joyner–Halenda methods, respectively, using an ASAP 2020 instrument (Micromeritics Instrument Corporation, Norcross, GA, USA). Prior to measurements, the samples were pretreated at 150 °C for 4 h under vacuum with N_2 gas exposure to remove impurities and moisture. Catalyst morphology was examined using field-emission scanning electron microscopy (JSM-7600, JEOL Ltd., Akishima, Japan), and Co distributions were determined using energy-dispersive X-ray spectroscopy (EDS). High-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) were performed using an aberration-corrected HR-(S)TEM instrument (JEM-2200FS, JEOL, 200 kV) to examine the nanoscale structure and morphology of the catalysts. The chemical states of surface elements were probed by X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo Fisher Scientific, USA) using $\text{Al K}\alpha$ radiation ($\lambda = 1.4866 \text{ \AA}$), with binding energies calibrated using the C 1s peak at 284.6 eV. Temperature-programmed reduction with H_2 (H_2 -TPR), temperature-programmed desorption of O_2 (O_2 -TPD), and N_2O -TPD measurements were conducted using a chemisorption analyzer (AutoChem II 2920, Micromeritics, USA) by increasing the temperature from 100 °C to 700 °C at a rate of 10 °C min⁻¹. For O_2 -TPD, the heating step was carried out either under N_2 or under continuous O_2 flow to evaluate atmosphere-dependent oxygen desorption behavior. In situ diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded using a Fourier transform infrared spectrometer (Vertex 80v, Bruker, USA) equipped with a Harrick DRIFT cell and liquid N_2 -cooled mercury cadmium telluride detector. The analyses were carried out under a continuous flow of 1000 ppm N_2O + 5% O_2 in N_2 (500 sccm). N_2O adsorption was performed at 50 °C, followed by temperature-programmed measurements under the same feed from 100 to 450 °C in 50 °C steps to track the evolution of surface species.

3.4. Catalytic Performance Test

N_2O conversion performance was evaluated in a fixed-bed quartz reactor with an inner diameter of 12.7 mm and a length of 400 mm. The feed-gas flow rate was controlled using mass flow controllers (Brooks Instruments, Hatfield, PA, USA). The reactant gas mixture consisted of 5000 ppm N_2O , 5% O_2 (when used), 500 ppm NO (when used), 5% H_2O (when used), and balance N_2 , with a total flow rate of 500 mL min⁻¹. The reactant

gases were supplied using commercially available mixed-gas cylinders and introduced through the mass flow control system. Water vapor was introduced by metering liquid water with a liquid pump (NEXT 109M, NEXT COMPANY Ltd., Gwangmyeong, Republic of Korea), followed by vaporization into the reactant stream. Powdered catalysts were loaded in an amount corresponding to 0.5 mL, giving a gas hourly space velocity (GHSV) of 60,000 h⁻¹.

Catalytic tests were conducted over the temperature range of 300–550 °C. The reactor temperature was continuously measured in real time using thermocouples connected to the fixed-bed reactor control program, and the temperature profile was monitored and recorded through the reactor monitoring system. To reflect the temperature near the catalyst bed as accurately as possible, the thermocouples were positioned at the upper part of the quartz reactor, as close as possible to the catalyst zone. Prior to entering the reactor, the feed-gas composition was adjusted in a bypass line and then switched to the reactor line for catalytic evaluation. The inlet and outlet concentrations of gases other than O₂ were analyzed using Fourier transform infrared spectroscopy (CX-4000, Gasmeter, Vantaa, Finland), while the O₂ concentration was monitored using a gas analysis spectrometer (DSM-XT, Hausnet S.R.L., Buenos Aires, Argentina). N₂O conversion was calculated as follows:

$$\text{N}_2\text{O conversion (\%)} = \frac{[\text{N}_2\text{O}]_{\text{in}} - [\text{N}_2\text{O}]_{\text{out}}}{[\text{N}_2\text{O}]_{\text{in}}} \times 100$$

where [N₂O]_{in} and [N₂O]_{out} are the inlet and outlet N₂O concentrations, respectively.

For the determination of apparent activation energy, kinetic measurements were carried out under high-GHSV and low-conversion conditions to minimize transport limitations. The experiments were performed under a feed containing 5000 ppm N₂O, 5% O₂ (when used), and N₂ balance at a GHSV of 500,000 h⁻¹. Since the catalytic activities differed among the samples, the catalyst amount and temperature range were adjusted for each catalyst to obtain reliable kinetic data within an appropriate conversion range. Specifically, the catalyst amounts used were 0.03 g for Co/Beta, 0.143 g for Co/CeO₂, 0.044 g for Co/TiO₂, and 0.134 g for Co₃O₄, while the temperature ranges were 300–450 °C for Co/Beta, 450–550 °C for Co/CeO₂, 450–650 °C for Co/TiO₂, and 350–500 °C for Co₃O₄, with 25 °C intervals. The reaction rate constant was derived from the measured N₂O conversion, and the apparent activation energy was determined from the slope of the corresponding Arrhenius plot.

4. Conclusions

Co-based catalysts supported on Beta zeolite, CeO₂, and TiO₂, together with unsupported Co₃O₄, were comparatively evaluated for direct N₂O decomposition under O₂-containing conditions. Among the tested catalysts, Co/Beta exhibited the highest activity and the best O₂ tolerance, achieving >95% N₂O conversion at 450 °C in the presence of 5% O₂ and maintaining stable performance during long-term operation. In contrast, Co/CeO₂ and Co₃O₄ showed clear O₂-induced inhibition, whereas Co/TiO₂ exhibited intrinsically low activity with little additional change upon O₂ introduction.

The superior performance of Co/Beta was associated with its favorable surface and structural characteristics. XPS analysis revealed that Co/Beta possessed the highest Co²⁺/(Co²⁺ + Co³⁺) ratio and the largest fraction of chemisorbed oxygen species, while H₂-TPR, O₂-TPD, N₂O-TPD, and in situ DRIFTS analyses consistently indicated enhanced oxygen mobility, facile oxygen turnover, and stable surface reaction behavior under O₂-containing conditions. These features contributed to suppressing O₂-induced inhibition and sustaining N₂O decomposition activity.

Additional coexisting-gas tests showed that Co/Beta retained high stability in the presence of O₂ and NO, while H₂O caused reversible inhibition. Overall, these findings demonstrate that support-dependent control of cobalt surface states and oxygen behavior is a key factor in achieving stable N₂O decomposition under oxygen-containing conditions, and that Co/Beta is a promising catalyst for practical N₂O abatement in semiconductor and display manufacturing processes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16050384/s1>, Figure S1: Field-emission scanning electron microscopy images and Co distributions of (a) Co/Beta, (b) Co/CeO₂, (c) Co/TiO₂, and (d) Co₃O₄; Figure S2: Particle-size distribution of bulk Co₃O₄ calculated from TEM measurement; Figure S3: HAADF-STEM-EDS elemental mapping images of (a) Co/Beta, (b) Co/CeO₂, (c) Co/TiO₂, and (d) Co₃O₄; Figure S4: N₂O conversion as a function of O₂ concentration for Co₃O₄ Reaction condition: 5000 ppm N₂O, O₂ (2.5–20%), N₂ balance, GHSV = 60,000 h^{−1}; Figure S5: Arrhenius plots for N₂O decomposition over (a) Co/Beta, (b) Co/CeO₂, (c) Co/TiO₂, and (d) Co₃O₄ catalysts; Figure S6: N₂O decomposition performances of (a) Co/Beta, (b) Co/CeO₂, (c) Co/TiO₂, and (d) Co₃O₄ under various conditions, namely 500 ppm N₂O, 5% O₂ (when used), 500 ppm NO (when used), 5% H₂O (when used) N₂ balance, GHSV = 60,000 h^{−1}.

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

Abbreviations

The following abbreviations are used in this manuscript:

L-H	Langmuir–Hinshelwood
E-R	Eley–Rideal
E _a	Apparent activation energy
XRD	X-ray diffraction
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
SEM	Scanning electron microscopy
EDS	Energy-dispersive X-ray spectroscopy
TEM	Transmission electron microscopy
HR-TEM	High-resolution transmission electron microscopy
STEM	Scanning transmission electron microscopy
HAADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
H ₂ -TPR	H ₂ temperature-programmed reduction
O ₂ -TPD	O ₂ temperature-programmed desorption

N ₂ O-TPD	N ₂ O temperature-programmed desorption
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
FTIR	Fourier transform infrared spectroscopy
GHSV	Gas hourly space velocity

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