Effect of Calcination Temperature on the Activation Performance and Reaction Mechanism of Ce–Mn–Ru/TiO₂ Catalysts for Selective Catalytic Reduction of NO with NH₃

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ABSTRACT: In this study, anatase TiO₂-supported cerium, manganese, and ruthenium mixed oxides (CeO₂−MnO₂−RuO₂/TiO₂; CMRT catalysts) were synthesized at different calcination temperatures via conventional impregnation methods and used for selective catalytic reduction (SCR) of NO with NH₃. The effect of calcination temperature on the structure, redox properties, activation performance, surface-acidity properties, and catalytic properties of the CMRT catalysts was investigated. The results show that the CMRT catalyst calcined at 350 °C exhibits the most efficient low-temperature (<120 °C) denitration activity. Moreover, the selective catalytic oxidation (SCO) reaction of ammonia is intensified when the reaction temperature is >200 °C, which leads to a decrease in the N₂ selectivity of the CMRT catalysts and further results in an increase in the production of NO and N₂O byproducts. X-ray photoelectron spectroscopy and in situ diffuse reflectance infrared Fourier transform spectroscopy show that the CMRT catalyst calcined at 350 °C contains more Ce⁴⁺, Mn⁴⁺, Ru⁴⁺, and lattice oxygen, which greatly improve the catalyst’s ability to activate NO that promotes the NH₃-SCR reaction. The Ru⁴⁺ sites of the CMRT catalyst calcined at 250 °C are the competitive adsorption sites of NO and NH₃ molecules, while those of the CMRT catalyst calcined at 350 and 450 °C are active sites. Both the Langmuir–Hinshelwood (L–H) mechanism and the Eley–Rideal (E–R) mechanism occur on the surface of the CMRT catalyst at the low reaction temperature (100 °C).

1. INTRODUCTION

Nitrogen oxides (NO and NO₂)¹ are the primary pollutants responsible for air pollution, damage the ozone layer, and are capable of direct damage to human health.²,³ Therefore, the effective treatment of NOₓ is important from both environmental and social standpoints. Currently, the main source of NOₓ (NO accounts for >90%) in the atmosphere is nitrogen-containing fuels, such as coke powder and coal in power plants, industrial boilers, and smelters.⁴,⁵ Over the last decade, high-temperature denitration by V₂O₅-WO₃(MoO₃)/TiO₂ catalysts was the primary technology supporting the NH₃-selective catalytic reduction (SCR) in the terminal denitration process.⁶⁻⁸ However, the operational temperature of the catalysts is very high at 300–400 °C.⁹⁻¹¹ Additionally, the temperature of the flue gas discharged from factories ranges from 100 to 120 °C following SO₂ removal, requiring reheating of the gas after desulfurization in sequence to grasp the operating temperature of the V₂O₅-WO₃(MoO₃)/TiO₂ catalyst.¹²,¹³ This increases both the construction costs for and power consumption of the plant. Therefore, the development of low-temperature (<120 °C) NH₃-SCR denitration technology is critical to achieving environmental protection requirements.

In recent years, cerium has attracted enormous attention because of the robust oxygen-transport capability between CeO₂ and Ce₂O₃ and high oxygen-storage ability of CeO₂.¹⁴,¹⁵ Additionally, manganese-element oxides and manganese-compound oxides have shown promising low-temperature denitration activity.¹⁶ However, the activity of Mn-based catalysts can still be greatly improved by doping with rare-earth metals or noble metals. Furthermore, some researchers have explored several SCR reaction mechanisms: (1) adsorbed NO species reacts with adsorbed NH₃ species on the surface of the catalyst and then decays into N₂ and H₂O (L–H mechanism), (2) activated NH₃ species on the surface of the catalyst reacts with gaseous NO and subsequently decomposes into the reaction products (E–R mechanism), or (3) the “fast SCR” mechanism (NO + NO₂ + NH₃ → N₂ + 3H₂O).¹⁷ Interestingly, these mechanisms are all premised on the
occurrence of the Mars–van Krevelen (M–K) mechanism that after the reaction between the reaction gas and the oxygen on the surface of the catalyst, the partly reduced surface is re-oxidized by O2.9,15 The M–K mechanism is a decisive factor affecting the activation of the reaction gas by the catalyst. Unfortunately, many researchers are not good at using the M–K mechanism to prepare catalysts and to explore the role of this mechanism in the field of SCR.

The element Ru is the cheapest noble metal and also the element with the largest number of oxidation states and surface defects, as well as a strong ability to resist corrosion and As poisoning. Moreover, RuO2 can remove Cl deposits on the surface of transition metals so as to keep up the activity of a catalyst.20,21 Furthermore, RuO2 exhibits a strong catalytic oxidation performance22 and has been extensively studied in the selective catalytic oxidation (SCO) field. For example, HCl can be catalytically oxidized by Ru-containing catalysts to produce Cl2 (the Deacon process).23 The activation performance of the catalyst is significant within the catalytic action of the catalyst. The process of the reaction gas being activated by the catalyst is that the catalyst uses O2 to catalytically oxidize the reaction gas into specific active intermediate products on its surface. Also, the activation process greatly reduces the activation energy of the SCR reaction, which is the reason the reaction will occur at low temperatures. Given the importance of SCO within the SCR reaction, RuO2 was used to modify the activation performance (selective catalytic oxidation performance) of the CeO2–MnO2/TiO2 catalyst.

In this study, a highly effective CeO2–MnO2–RuO2/TiO2 (CMRT) catalyst was synthesized based on the M–K mechanism using CeO2, MnO2, and RuO2 as active metal oxides and commercial anatase TiO2 powder as a support, which contains abundant oxygen vacancies, Lewis acid sites, and Bronsted acid sites.24 The effect of calcination temperature on the low-temperature denitration activity of the CMRT catalyst was first evaluated. Characterizations via X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), NH3 temperature-programmed desorption (NH3-TPD), NO + O2 temperature-programmed desorption (NO + O2-TPD), and in situ diffuse reflectance infrared (IR) Fourier transform spectroscopy (in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)) were performed to elucidate the mechanisms of various denitrification activities of the CMRT catalysts calcined at different temperatures and the low-temperature NH3-SCR reaction mechanism of the CMRT catalyst.

2. RESULTS AND DISCUSSION

2.1. Effect of Calcination Temperature on Catalytic Activity. Figure 1a shows the NH3-SCR activities of the CMRT-X (X = 250, 300, 350, 400, 450 °C) catalysts calcined at different temperatures. CMRT-350 exhibits the highest low-temperature denitration activity. The deNOx activity of CMRT-300 is similar to that of CMRT-350. However, when the calcination temperature of the CMRT catalyst rises to 450 °C, the NOx conversion is remarkably reduced. When the reaction temperature is 100 °C, the NOx conversion of the CMRT-450 is only 80%, whereas CMRT-350 shows a >95% NOx conversion at 100 °C and nearly 100% NOx conversion at between 120 and 250 °C. Additionally, the denitrification activities of CMRT-250 and CMRT-400 are similar. Moreover, the stability of the catalyst is an important indicator for evaluating the catalyst. Thus, the CMRT-350 catalyst was tested at 120 °C for 72 h, and its corresponding activities are shown in Figure 1b. It is clear that changes of the NOx conversion of the CMRT-350 catalyst maintain above 99% at 120 °C for 72 h, indicating that the CMRT-350 catalyst has an excellent catalytic stability in the NH3-SCR reaction. Figure S1 shows the N2 selectivity of the CMRT-X catalysts, and all samples show a similar trend. As the reaction temperature increases, the N2O and NO byproducts increase due to the intensification of ammonia oxidation, resulting in a decrease in the N2 selectivity of the catalyst. This will be discussed further in the results of NO + NH3 + O2− in situ DRIFTS and NH3 oxidation.

Furthermore, SO2 was added into the original reaction gas to test the denitration performances at 120 °C of the CMRT-250, 350, and 450, and the results are illustrated in Figure S2. It is markedly observed in Figure S2 that when SO2 is added, the denitration activity of the CMRT catalysts decreases from >97 to <28% at 120 °C. This may be because most of the active sites on the surface of the catalysts are firmly occupied and poisoned by SO2 species.25 In addition, the denitration activity of the CMRT-350 catalyst is significantly higher than that of CeO2/TiO2 (CT), CeO2–RuO2/TiO2 (CRT), and CeO2–MnO2/TiO2 (CMT) catalysts calcined at 350 °C and TiO2 powder (T) (Figure S3). This may be due to the contribution of the strong synergistic effect between Ce, Ru, and Mn.
2.2. Effect of Calcination Temperature on the Catalyst Structure. The X-ray diffraction (XRD) patterns of the CMRT-X catalysts are displayed in Figure 2. Low-intensity diffraction peaks of RuO$_2$ and anatase TiO$_2$ in all composite oxides can be observed, whereas no diffraction peaks for Ce or Mn species are present, clearly indicating that the Ce and Mn oxides as homogeneous microcrystals or clusters are well dispersed on the TiO$_2$ surface. The peaks at 25.3, 37.8, 48.0, 53.9, 55.1, 62.7, and 75.0° correspond to (101), (004), (200), (105), (211), (204), and (215) of anatase (JCPDS 21-1272), respectively, and those at 28 and 35° correspond to (110) and (101) of RuO$_2$, respectively. There are two unsaturated coordination sites on the RuO$_2$ (110) crystal plane, namely, Ru unsaturated coordination site (Ru$_{pu}$) and bridge O (O$_b$). Ru$_{pu}$ has a strong adsorption capacity for reactive gas molecules, and the adsorbed reactive gas molecules can react with O$_b$ at low temperatures. Therefore, both the undercoordinated sites are considered to be the catalytically active surface sites of RuO$_2$ (110). In addition, the RuO$_2$ (110) crystal plane displays strong oxidation performance, which is widely studied in the fields of catalytic oxidation of HCl, NH$_3$, methanol, CO, and CH$_4$. Few studies reported a RuO$_2$ (101) crystal plane structure and redox properties for a very low exposure ratio of the RuO$_2$ (101) crystal plane. The average crystal sizes (Table 1) of all samples were estimated by the diffraction peak based on the Scherrer formula. This shows that as the calcination temperature increases, the crystal sizes of the CMRT-X catalysts first decrease and then increase. The appropriate crystal size of CMRT-350 could potentially increase the strength of the interaction between the active phase and the support, thereby promoting easier oxidation of the active phases Ce, Mn, and Ru. In addition, images (Figure S4) of scanning electron microscopic (SEM) and energy-dispersive spectrometry (EDS) mapping of CMRT-350 show the dispersion properties of Ce, Mn, Ru, O, and Ti elements. This clearly shows that the Ce, Mn, Ru, O, and Ti atoms are well distributed on the surface of the catalyst.

The specific surface areas of the CMRT-X catalysts are shown in Table 1. The results indicate that the specific surface areas of the CMRT-X catalysts increase slowly at first and then rapidly weaken beside a rise with the calcination temperature. For instance, the specific surface areas of CMRT-250, 300, 350, and 450 are ~81.0, ~83.8, and 63.0 m$^2$ g$^{-1}$, respectively. This result is in agreement with the trend of the crystallite size. When the calcination temperature is >350 °C, the specific surface areas of CMRT catalysts decrease, which may be because the oxides in the catalyst begin to sinter. CMRT-350 shows the largest specific surface area among the synthesized catalysts. This may end in the strongest activation capacities of CMRT-350 for the NO, which promotes the NH$_3$-SCR reaction. This will be discussed further in the results of NO + O$_2$-TPD and in situ DRIFTS.

The H$_2$-TPR results are displayed in Figure S5. It can be clearly observed that as the calcination temperature increases, the peak temperatures of the CMRT-X catalysts reduced by H$_2$ gradually increase. It is possible that the adsorption capacity of CMRT catalysts for H$_2$ and their completely different structures as well have an effect on the reduction performance of CMRT catalysts.

2.3. Effect of Calcination Temperature on the Surface Valence and Redox Properties of the Catalysts. The surface atomic proportions and chemical valence distributions were analyzed by XPS, with the Ce 3d, O 1s, Ru 3d, and Mn 2p spectra and their deconvoluted fitting curves shown in Figure 3. The core-level spectrum of Ce 3d, of the CMRT-X catalysts is shown in Figure 3a, and the complex spectra comprising both Ce$^{3+}$ and Ce$^{4+}$ states were deconvoluted into eight peaks: one doublet for CeO$_2$ (Ce$^{3+}$) and three doublets for CeO$_2$ (Ce$^{4+}$). The six characteristic peaks for Ce$^{4+}$ were labeled V$_0$ (882.3 ± 0.1 eV), V$_1$ (888.9 ± 0.1 eV), V$_2$ (898.4 ± 0.1 eV), U$_0$ (901.4 ± 0.1 eV), U$_1$ (907.8 ± 0.1 eV), and U$_2$ (916.7 ± 0.2 eV), with the bands labeled V$_1$ (888.8 ± 0.1 eV) and U$_1$ (904.4 eV) arising from Ce$^{3+}$. The ratio of Ce$^{4+}/$(Ce$^{3+}$ + Ce$^{4+}$) was calculated using the corresponding peak areas to decode an alteration in the chemical state of Ce caused by different calcination temperatures. As manifested in Table 2, the Ce$^{4+}/$(Ce$^{3+}$ + Ce$^{4+}$) ratio rises from 61.94% (CMRT-250) to 64.14% (CMRT-350) and then decreases to 63.11% (CMRT-450), indicating that Ce$^{4+}$ is a predominant oxidation state. Additionally, the detected redox switch and oxygen defects affecting the coexistence of Ce$^{4+}$ and Ce$^{3+}$ are conducive to low-temperature NH$_3$-SCR. According to refs 1734–1736, the introduction of CeO$_2$ into the MnO$_x$/TiO$_2$ catalyst can increase the Mn$^{3+}$ content. CeO$_2$ has a strong ability to store oxygen, but the low-temperature denitration ability of CeO$_2$ is poor (Figure S3), so it acts more as an auxiliary catalyst to convert a large amount of Mn$^{3+}$ into Mn$^{4+}$. Hence, before Ce$^{4+}$/Ce$^{3+}$ reaches an optimal ratio, a higher relative content of CeO$_2$ will result in an expansion ability of the catalyst to store lattice oxygen. These findings indicate that CeO$_2$ promotes the transition from Mn$^{3+}$ and Mn$^{4+}$ to Mn$^{4+}$ described in eq 1 and may promote that from Ru$^{3+}$ to Ru$^{4+}$ shown in eq 2, both of which strengthen the M–K mechanism and activation performance of the catalyst.

### Table 1. Specific Surface areas, Total Pore Volumes, and Crystallite Sizes of CMRT Catalysts Calcined at Different Temperatures

| sample | specific surface areas (m$^2$ g$^{-1}$) | crystallite size (nm) |
|--------|----------------------------------------|-----------------------|
| CMRT-250 | 81.0 | 16.5 |
| CMRT-300 | 81.5 | 16.4 |
| CMRT-350 | 83.8 | 16.2 |
| CMRT-400 | 71.2 | 16.6 |
| CMRT-450 | 63.0 | 16.9 |
The Mn 2p XPS peaks were deconvoluted into four peaks for the CMRT-X catalysts (Figure 3b), with the peaks at 640.3 ± 0.1, 641.3 ± 0.1, and 642.7 eV ascribed to Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$, respectively, and that at 645 ± 0.1 eV representing the satellite peak of Mn. As indicated in Table 2, the value of the Mn$^{3+}$/Mn (Mn$^{2+}$ + Mn$^{3+}$ + Mn$^{4+}$) in the surface layer of the CMRT-X catalysts initially increases from 42.43% (CMRT-250) to 50.81% (CMRT-350) and then decreases to 43.46% (CMRT-450) along with escalating oxidation temperature, indicating that the Mn$^{4+}$ oxidation state is predominant.

Kapteijn et al. have suggested that the NO conversions alleviated in the order of MnO$_2$ > Mn$_5$O$_8$ > Mn$_2$O$_3$ > Mn$_3$O$_4$ between 385 and 575 K. Additionally, Tang et al. showed that a lot of Mn$^{4+}$ species and richer lattice oxygen species resulted in abundant higher catalytic oxidation activity. Since the catalytic oxidation process is based on the M–K mechanism, MnO$_2$ is extraordinarily beneficial to the redox performance of the catalyst. The lattice oxygen of MnO$_2$ participates in the activation process of the reaction gas and is expressed as formulas 3 and 6, and then Mn$_2$O$_3$ and MnO are re-oxidized to MnO$_2$ by the oxygen species provided by CeO$_2$ as shown in formula (10). Thus, MnO$_x$ is one of the main transport channels for the transfer of lattice oxygen (O$_2^-$) of the CMRT catalyst in the NH$_3$-SCR reaction. The increased MnO$_2$ concentration before Mn$^{4+}$/Mn$^{3+}$/Mn$^{2+}$ reaches the optimal ratio improves both the M–K mechanism and activation performance of the CMRT catalyst.

As presented in Figure 3c, the Ru 3d XPS spectra were divided into a Ru$^{4+}$ cation peak appearing at 281.2 ± 0.1 eV. The Ru$^{4+}$ content of the CMRT catalysts initially expands and then shrinks along with the rising calcination temperature, and the CMRT-350 contains the most Ru$^{4+}$ (Table S1), indicating that the Ru$^{4+}$ content exerts a critical effect on catalyst activity.
Because RuO$_2$ has abundant oxygen vacancies and surface defects,$^{40}$ the adsorption and removal of surface oxygen and the M$^-$K mechanism of the CMRT catalyst are strengthened.$^{41}$ Therefore, the redox performances of CeO$_{x}$ and MnO$_{x}$ are improved at low temperatures, while, additionally, the overall catalytic oxidation performance of the catalyst is greatly enhanced. Moreover, RuO$_{x}$ and CeO$_{x}$ establish a second O$_2^-$ transport channel of the CMRT catalyst, described in eq 2.

The deconvoluted O 1s XPS spectra of the CMRT-X catalysts are given in Figure 3d. All samples show two distinct peaks assigned to lattice oxygen (O$_{\alpha}$, denoted O$_{\alpha}$) at between 529.7 and 529.9 eV and surface-chemical-adsorbed oxygen species (O$_{2\alpha}$ or O$_{\beta}$, denoted O$_{\beta}$) at between 531.5 and 531.7 eV.$^{39}$ The atomic ratios of O$_{\alpha}$/O$_{\alpha}+O_{\beta}$ on the surface of these catalysts were calculated and are exhibited in Table 2. It is significant that the atomic ratios of O$_{\alpha}/(O_{\alpha}+O_{\beta})$ for the CMRT catalysts increase initially and then decrease along with the increasing calcination temperature and that CMRT-350 displays the highest O$_{\alpha}/(O_{\alpha}+O_{\beta})$ value (76.45%), suggesting the predominance of the crystal lattice oxygen (O$_{\alpha}$). Lee et al.$^{42}$ also published that the lattice oxygen of the Mn/TiO$_2$ catalyst powerfully affects the low-temperature SCR reaction. Zheng et al.$^{43}$ outlined that the activated nitrate species adsorbed on the catalyst surface is produced by the reaction of NO and lattice oxygen, and a similar result was ascertained by in situ DRIFT in this study. Based on the M$^-$K mechanism, NO and NH$_3$ molecules react with lattice oxygen on the surface of the high-valent metal oxide to generate several active intermediates, followed by reduction of the high-valent metal oxide in the catalyst to a low-valent state (from MnO$_{m}$ to MnO$_{m-\delta}$. M denotes the transition metals).$^{41}$ This is followed by the transition of the gas-phase oxygen adsorbed on the catalyst surface to lattice oxygen and re-oxidation of the low-valent metal oxide back to the initial high-valent state, thereby completing the redox cycle.$^{44}$ These clearly indicate that the increase of lattice oxygen can directly and greatly enhance the oxidation–reduction performance of the CMRT catalyst, accelerating the generation and mutual reaction of active intermediates such as nitrate and amide, thereby improving the catalytic performance of the CMRT-X catalyst.

In summary, the CMRT-350 catalyst contains the most Ce$^{4+}$, Mn$^{4+}$, Ru$^{4+}$, and lattice oxygen, and this is not a coincidence. There should be a strong interaction between them so that they are all oxidized to the highest valence state. The CMRT-350 catalyst has the strongest redox performance, and this result is also directly proved by the following in situ DRIFT experiments.

2.4. Effect of Calcination Temperature on the Surface-Acidic Properties of the Catalysts. In the NH$_3$-SCR reaction, the NH$_3$-adsorption and -desorption ability of a catalyst and the degree of NH$_3$ activation on the catalyst surface are necessary parameters for analyzing the catalytic mechanism. Therefore, NH$_3$-TPD and NH$_3$ in situ DRIFTS were accustomed to investigating the relative quantity distribution of the surface acid content of the CMRT-X catalysts and NH$_3$ adsorption form on the catalyst surface. The
NH₃-TPD characterization of the CMRT-X catalysts at completely different oxidation temperatures is presented in Figure 4a. The results of NH₃ in situ DRIFTS for CMRT-250, -350, and -450 are shown in Figure 4b−d. Figure 4a shows that the main NH₃-desorption temperature of the CMRT-X catalysts is <100 °C, indicating that NH₃ is mainly physically

Figure 5. NO + O₂-TPD patterns (a) and in situ DRIFTS of NO + O₂ adsorption spectra recorded at 100 °C with time on CMRT-250 (b), CMRT-350 (c), and CMRT-450 (d) samples.
assimilated on the catalyst surface. The order of NH₃ desorption is 250 > 350 > 300 > 400 > 450, which does not correspond to the order of activity of the CMRT-X catalysts. This indicates that the quantity of NH₃ adsorption is not the key factor affecting CMRT catalyst activity. Prior to testing NH₃ in situ DRIFTS, the samples were pretreated in N₂ at 200 °C for 1 h, followed by cooling to 100 °C and injection of 550 ppm NH₃/N₂ into the reaction chamber. IR spectra were then recorded as a function of time (0, 3, 10, 20, 30, 40, 50, and 60 min).

The NH₃ species adsorbed on the surfaces of CMRT-250, -350, and -450 displayed similar adsorption spectra (bands at 3334−3257, 1843, 1593, 1558, 1553, 1437, 1344, 1339, 1297, 1266, and 1211 cm⁻¹) (Figure 4b–d). The bands centered at around 3334−3257 cm⁻¹ were allocated to the overlap bands of N−H-vibrated coordination of NH₃ and M−OH (M denotes to the transition metals). The bands at 1593, 1297, 1266, and 1211 cm⁻¹ were accredited to N−H vibrations linked to Lewis acid sites (marked as L-acid sites). The bands at 1558, 1553, 1344, and 1339 cm⁻¹ were related to the scissoring vibration mode of NH₂ species. The band at 1437 cm⁻¹ was assigned to NH₄⁺ species associated with Brønsted acid sites, and the band at 1843 cm⁻¹ was assigned to NH₃ molecules adsorbed on Ru⁺. Based on NH₃-DRIFTS results, the amounts of NH₃-active species adsorbed on the surface of CMRT-250, -350, and -450 are sorted as 250 > 350 > 450, indicating that the adsorption strength of NH₃ on the catalyst surface is not positively related to catalyst activity. Therefore, NH₃ adsorption and activation are all not the rate-limiting steps of NH₃-deNOₓ of CMRT-X catalysts.

2.5. Effect of Calcination Temperature on NO Adsorption and Activation of the Catalysts. To further investigate the mechanism of NH₃-SCR, we used NO+O₂−TPD and NO + O₂ in situ DRIFTS to evaluate the NO-adsorption and -activation properties of the CMRT-X catalysts. NO + O₂−TPD analysis and the Fourier transform IR spectra of NO + O₂ adsorption for the CMRT-X samples are presented in Figure 5. The samples and pretreatments for the NO + O₂ in situ DRIFTS experiments were the same as those described for NH₃ in situ DRIFTS, followed by injection of 550 ppm NO/N₂ and 10% O₂ into the reaction chamber and spectra recorded as a function of time (0, 3, 10, 20, 30, 40, 50, and 60 min).

Figure 5a shows that the order of NO desorption based on integrated areas is 250 > 300 > 350 > 400 > 450. The NO desorption capacity of the CMRT-450 catalyst is not the lowest, but its activity is the lowest, which indicates that single NO adsorption does not determine the catalytic activity of catalysts. Additionally, the order of NO₂ desorption following CMRT catalysts using O₂ to catalytically oxidize NO is 250 > 300 > 350 > 400 > 450, indicating that the production of NO₂...
Figure 7. In situ DRIFTS spectra recorded at 100 °C upon passing NH3 over NO + O2 presorbed on CMRT-250 (a), CMRT-350 (b), and CMRT-450 (c) samples with time.

is not the main factor affecting catalyst activation either. It can be confirmed that the mechanism of CMRT-X catalysts is not fast SCR. Moreover, adsorption of NO + O2 on the surface of three CMRT catalysts resulted in the formation of eight NO active species: bridged nitrate (1250 and 1606 cm⁻¹), monodentate nitrates (1286 and 1488, cm⁻¹), M⁺⁻NO₂⁻ species (1315–1350 cm⁻¹), unstable N₂O₄ species (1521 and 1522 cm⁻¹), ionic nitrates (1457 and 1473 cm⁻¹), bidentate nitrates (1506, 1540, 1555, 1558, and 1583 cm⁻¹), Ru⁺⁻NO molecules (1890 cm⁻¹), M⁺⁻H₂O (1715–1866 cm⁻¹), and adsorbed NO species (1158 cm⁻¹) (Figure 5b–d). These results suggest that the CMRT-350 catalyst adsorbs most types and amount of NO active species, indicating that the reaction between NO and O₂ is most active on the surface of CMRT-350. The amount of NO species adsorbed on the CMRT-450 surface is less than that of CMRT-350, indicating that the degree of NO and O₂ activation on the CMRT-450 surface is inferior to that of CMRT-350. Interestingly, the NO+O₂ IR spectrum of CMRT-250 differs from that of the others. First, the number of active NO species adsorbed by CMRT-250 (1606–1433 cm⁻¹) is less than that by CMRT-350, whereas the number of other active NO species (1606–1570 and 1413–1307 cm⁻¹) is higher than that by CMRT-450. Second, the NO molecular-adsorption peak on Ru⁺⁺ on CMRT-250 at 1890 cm⁻¹ is clear, whereas the other two catalysts show minimal intensity at 1890 cm⁻¹. This may be due to the competitive adsorption of NO and O₂ on the Ru⁺⁺ site of CMRT-250, with NO preferentially adsorbed and occupying most of the active sites and resulting in insufficient active sites remaining for O₂ adsorption. Therefore, the activation of the adsorbed NO molecules is prevented.

Because of the inability of NO adsorbed on the catalyst surface to form nitrate species, oxidation of NO to NO₂ was the only way to form nitrate species. Therefore, based on the difference in NO + O₂ in situ DRIFTS results for CMRT-250, -350, and -450, the order of NO activation performance on the catalyst surface is 350 > 250 > 450, which is similar to the trend observed for their respective low-temperature denitration activities (Figure 1). These results clearly show that the main factor affecting CMRT-X activity is the degree of NO activation on the catalyst surface.

2.6. Reaction between NOx and Pre-adsorbed NH₃ Species on the CMRT Catalyst Surface. To more explore the mechanism of NH₃-SCR, we performed in situ transient reactions. After similar pretreatment methods to those used for NH₃ in situ DRIFTS, all catalysts were cooled at 100 °C, treated with 550 ppm NH₃/N₂ for 1 h, and then purged with N₂ for 1 h. After injection of 550 ppm NO and 10% O₂, spectra were recorded as a function of time (0, 3, 10, 20, 30, 40, 50, and 60 min) (Figure 6).

On the passage of NH₃ into the in situ cell, adsorption peaks similar to those determined by NH₃ in situ DRIFTS were observed. Following the addition of NO + O₂ bands related to
L- and B-acid sites, NH₃ molecules, OH, and NH₂ all disappear within 30 min, whereas bands at 1890 cm⁻¹ (Ru⁺⁺-NO₃ molecules), 1606 cm⁻¹ (bridged nitrate), 1540–1583 cm⁻¹ (bidentate nitrate), 1337 and 1286 cm⁻¹ (NH₄NO₂ species), 1250 cm⁻¹ (bridged nitrate), and 1158 cm⁻¹ (NOₓ species) are observed. This suggests that all of the NHₓ species adsorbed on the catalyst surface join in the reaction. Additionally, different characteristic NOₓ-adsorption peaks for CMRT-350 and -450 are observed at 30 min after NO + O₂ injection, whereas the bands are observed after 50 min for CMRT-250. This suggests that the NHₓ species adsorbed onto CMRT-350 and -450 react more easily with NOₓ active species than on CMRT-250, and CMRT-250 exhibits a particularly strong adsorption capacity for NH₃. Moreover, after the NH₃ molecules (1843 cm⁻¹) adsorbed on the Ru⁺⁺ site of CMRT-250 are consumed by incoming NO + O₂, the NO molecules are re-adsorbed on the Ru⁺⁺ site (1890 cm⁻¹) as an E−R mechanism (eqs 3 and 5). This identifies the Ru⁺⁺ site as the competitive adsorption site for NO and NH₃ molecules. However, no competitive adsorption of NH₃ and NO molecules is found on the Ru⁺⁺ sites of CMRT-350 and -450; therefore, the Ru⁺⁺ sites on these two catalysts represent active sites rather than competitive adsorption sites. Because CMRT-450 shows the worst adsorption and activation capacities for NH₃, the reactivity of NH₃ species with NOₓ active species (L−H) and with NOₓ(g) (E−R) is reduced, resulting in poor CMRT-450 activity (the reaction route of the L−H mechanism is shown in eq 7). Furthermore, the comparison of the advantages and disadvantages of reactions between NO + O₂ and preadsorbed NHₓ species on the surface of the three catalysts reveals that the competitive adsorption of NO and NH₃ occurs on the surface of CMRT-250 and it is easily poisoned by NHₓ. However, CMRT-350 shows neither competitive adsorption nor NH₃ poisoning and displays the strongest activation capacity for NO and O₂. Thus, CMRT-350 exhibits the highest catalytic activity.

2.7. Reaction between NHₓ and Pre-adsorbed NOₓ Species on the CMRT Catalyst Surface. Following the previously described pretreatment methods for NH₃ in situ DRIFTS, the CMRT catalysts were cooled to 100 °C, injected with 550 ppm NO and 10% O₂ for 1 h, and purged with N₂ for 1 h. Subsequently, 550 ppm NH₃/N₂ was introduced, and
spectra were recorded as a function of time (0, 3, 10, 20, 30, 40, 50, and 60 min) (Figure 7). The introduction of NO and O2 results in bands at 1890 cm\(^{-1}\) (Ru\(^{+}\)-NO molecules), 1606 cm\(^{-1}\) (bridged nitrate), 1540 and 1583 cm\(^{-1}\) (bidentate nitrate), 1337 cm\(^{-1}\) (M\(^{+}\)\(\cdot\)NO\(_2\) species), 1286 cm\(^{-1}\) (monodentate nitrate), 1250 cm\(^{-1}\) (bridged nitrate), and 1158 cm\(^{-1}\) (NO\(_3\) species). Following the addition of NH\(_3\), the peak densities (at 1890, 1606, 1583, 1337, 1250, and 1158 cm\(^{-1}\)) decrease dramatically and ultimately disappear, and the band at 1286 cm\(^{-1}\) is overlaid with 1293 cm\(^{-1}\) (NH\(_4\)NO\(_2\) species).\(^{17}\) After 60 min, characteristic adsorption bands are observed for NH\(_3\) at 3334–3257 cm\(^{-1}\) (N–H vibrated coordinated NH\(_3\) and M–OH), 1843 cm\(^{-1}\) (Ru\(^{+}\)\(\cdot\)NH\(_3\) molecules), 1593 cm\(^{-1}\) (L-acid sites), 1558 and 1553 cm\(^{-1}\) (NH\(_3\) species), 1457 cm\(^{-1}\) (NH\(_4\)NO\(_2\) species), 1437 cm\(^{-1}\) (B-acid sites), and 1226 cm\(^{-1}\) (NH\(_3\),NO\(_2\) species).\(^{17}\) It can be summarized in Figure 7a–c that the NO\(_x\) species adsorbed on CMRT-350 and -450 more easily react with NH\(_3\) than on CMRT-250 because they reach equilibrium within 10 min versus 20 min for CMRT-250. Additionally, Figure 7b shows that the number of reaction products generated by NH\(_3\) and the NO\(_x\) species preadsorbed on the surface of CMRT-350 is the most among the three catalysts, indicating that CMRT-350 displays the highest catalytic activity. Moreover, Figure 7a shows that after consumption of the 1890 cm\(^{-1}\) band (Ru\(^{+}\)-NO molecules) on CMRT-250 by NH\(_3\) the 1843 cm\(^{-1}\) band (Ru\(^{+}\)-NH\(_3\) molecules) was generated, indicating that Ru\(^{+}\) on CMRT-250 provides a competitive adsorption site for NO and NH\(_3\) molecules. Because it is impossible for NH\(_3\) and NO molecules to react directly, the reaction pathway between preadsorbed NO molecules and NH\(_3\) molecules at the Ru\(^{+}\) sites is followed by the L–H mechanism (eqs 3 and 7). However, no competitive adsorption of NH\(_3\) and NO is observed on the Ru\(^{+}\) sites of CMRT-350 or -450. This suggested that the Ru\(^{+}\) sites of the CMRT-250 are the competitive adsorption sites of NO and NH\(_3\) molecules, while those of the CMRT-350 and -450 are active sites.

2.8. NO + O\(_2\) + NH\(_3\) Coadsorption on the CMRT Catalyst Surface. Following pretreatment as previously described for NH\(_3\) in situ DRIFTS, the catalysts were cooled to 50 °C. Then, 550 ppm NO, 550 ppm NH\(_3\), and 10% O\(_2\) were administered to the reaction chamber and IR spectra were recorded with increasing temperature, and the results are illustrated in Figure 8. For CMRT-250, -300, and -350, peaks at between 3355 and 3263 cm\(^{-1}\) and also at 1173 cm\(^{-1}\) were allocated to the coordinated NH\(_3\) group,\(^{17}\) the band at 1843 cm\(^{-1}\) was linked to NH\(_3\) molecules at the Ru\(^{+}\) sites, B-acid sites were situated at 1442 cm\(^{-1}\), and bands at 1577 cm\(^{-1}\) were connected to NH\(_3\) species. Peaks at 1593, 1293, and 1173 cm\(^{-1}\) reference L-acid sites, and new strong bands between 1230 and 1496 cm\(^{-1}\) represented NH\(_4\)NO\(_2\) reaction intermediates,\(^{17}\) whereas bands at 2237 and 2207 cm\(^{-1}\) were assigned to N\(_2\)O molecules.\(^{49,62–65}\)

Interestingly, CMRT-250, -350, and -450 display no adsorption of NO\(_x\) species and only adsorption of NH\(_3\) species at low temperature (Figure 8a–c) according to the favorable adsorption of NH\(_3\) during competitive adsorption between NH\(_3\), NO, and O\(_2\). For CMRT-250, as the reaction temperature increased, there is no change in the band at 1843 cm\(^{-1}\) (Ru\(^{+}\)-NH\(_3\) molecules), indicating that when the catalyst simultaneously adsorbs NO + NH\(_3\) + O\(_2\), the Ru\(^{+}\) site is consistently occupied by NH\(_3\) molecules. However, when CMRT-250 adsorbs NH\(_3\) (Figure 4b) or NO + O\(_2\) (Figure 5b), its Ru\(^{+}\) site is occupied with NH\(_3\) or NO molecules, respectively. This again confirms that the Ru\(^{+}\) site of CMRT-250 undergoes competitive adsorption of NO and NH\(_3\) molecules and is susceptible to NH\(_3\) poisoning during the reaction. However, NH\(_3\) poisoning of the Ru\(^{+}\) site on CMRT-350 and -450 is not observed, suggesting that the Ru\(^{+}\) site of CMRT-250 does not take part in a catalytic role in the denitration reaction, whereas these sites on CMRT-350 and -450 promote catalytic activity. This is consistent with findings in Sections 2.6 and 2.7. Additionally, the formation speed and levels of the intermediate products NH\(_4\)NO\(_2\) (1230–1496 cm\(^{-1}\)) and N\(_2\)O (2207–2237 cm\(^{-1}\)) on the surface of the three substances at high reaction temperature (200–350 °C) follow the order of 450 > 350 > 250, indicating that a part of NO\(_x\) species is converted into NH\(_4\)NO\(_2\) and N\(_2\)O rather than N\(_2\). This also indicates that as the reaction temperature increases, the N\(_2\) selectivity of the CMRT-X catalysts reduces. On top of that, a higher calcination temperature produces larger amounts of NH\(_4\)NO\(_2\) and N\(_2\)O.

Furthermore, Figure 9 displays that the order of the ability of the CMRT catalysts to catalytically oxidize NH\(_3\) to NO using O\(_2\) at high temperature (200–350 °C) is 250 > 300 > 350 > 400 > 450. Generally, a higher ability to catalytically oxidize NH\(_3\) is more detrimental to the reaction.\(^{66}\) Thus, a higher calcination temperature decreases NH\(_3\) conversion to NO, making the catalyst more favorable for the denitration reaction. It is concluded that at reaction temperatures >200 °C, the reaction of NO\(_2\) and NH\(_3\) conversion to NH\(_4\)NO\(_2\) and N\(_2\)O is enhanced with the rise of calcination temperature, and NH\(_3\) conversion to NO is decreased (Figure 9). It shows that the NO\(_2\)-conversion capacity of the CMRT-X catalysts at >200 °C follows the order of 450 > 400 > 350 > 300 > 250, which corresponds to the activity sequence of the catalyst at >200 °C (Figure 1).

2.9. Proposed Mechanism. Scheme 1 describes the NH\(_3\)-SCR response mechanism for the CMRT-X catalysts at 100 °C. At a reaction temperature of 100 °C, CeO\(_2\) has almost no denitrification activity,\(^{17}\) so it is mainly used to store and transfer oxygen species to MnO\(_2\) and RuO\(_2\).\(^{58}\) Ru\(_{\text{cav}}\) on the surface of RuO\(_2\) is mainly used to adsorb reaction gas and
activate O$_2$ to generate oxygen unsaturation sites (O$_{\text{unsat}}$). Also, O$_{\text{unsat}}$ and O$_{\text{tr}}$ are activators for activating NO and NH$_3$ molecules on the surface of RuO$_2$.\textsuperscript{28} In addition, our experimental results also show that there is a competitive adsorption of NO and NH$_3$ molecules on the Ru$_{\text{n+}}$ sites of the CMRT catalyst calcined at 250 °C. The E−R and L−H mechanisms are described in eqs 3−7, the M−K mechanism is described in eqs 8−12, and the NH$_3$ oxidation reaction is described in eqs 13−15.

The M−K cycle is as follows:

CeO$_3$/MnO$_2$/RuO$_2$ $\rightarrow$ Ce$_2$O$_3$/MnO/RuO$_2$  \( (8) \)

O$_2(\text{ad})$ $\rightarrow$ O$_{\text{ads}}$ $\rightarrow$ O$_2$  \( (9) \)

MnO $\rightarrow$ Mn$_2$O$_3$ $\rightarrow$ MnO$_2$  \( (10) \)

Ce$_2$O$_3$ $\rightarrow$ CeO$_2$  \( (11) \)

RuO$_4$ $\rightarrow$ RuO$_2$  \( (12) \)

with the side reactions

NH$_2(\text{ad})$ + O $\rightarrow$ NO + H$_2$O (NH$_3$ oxidation)  \( (13) \)

NH$_2(\text{ad})$ $\rightarrow$ NH$_{\text{ads}}$ + H  \( (14) \)

NH$_{\text{ads}}$ + NO $\rightarrow$ N$_2$O + H (N$_2$O generation)  \( (15) \)

where O$_{\text{ads}}$ is the O$_2$ molecule adsorbed on the surface of the catalyst and O$_{\text{ads}}$ is related to the chemisorbed oxygen.

The M−K mechanism is the main mechanism associated with the CMRT-X catalysts, and the main participant in the M−K cycle is lattice oxygen (O$^{2−}$).\textsuperscript{53} The highest-valence metal oxides, such as MnO$_2$ and RuO$_2$, are the main activators of NO and NH$_3$. These results indicate that the entire M−K cycle uses O$^{2−}$ to connect the reaction gas, catalyst, and products in series; therefore, enhancing the O$^{2−}$ transfer ability will boost the catalytic performance of the catalyst.

For the NH$_3$-SCR reaction, in situ DRIFTS outcomes show that the activation capacity of the CMRT-X catalysts for NO species is crucial. In addition, nitrates adsorbed on the catalyst surface are the most significant activation products as well as the most important reactants in the SCR reaction.

At reaction temperatures $>$150 °C, ammonia oxidation decreases the denitration reaction and N$_2$ selectivity of CMRT catalysts. In addition, the amount of NH$_4$NO$_2$ and N$_2$O species increases as the reaction temperature rises.

**3. CONCLUSIONS**

In this study, a sequence of CMRT-X catalysts was synthesized using a wet co-impregnation method and at five different calcination temperatures. We observed that the decrease in the denitration activity of the CMRT catalysts at reaction temperatures $>$150 °C is due to excess NH$_3$ oxidation and generation of NO and N$_2$O byproducts. The catalytic mechanism of CMRT-catalysts is mainly the M−K mechanism, supplemented by the E−R mechanism and the L−H mechanism. These three mechanisms jointly promote the progress of the SCR response, and the O$^{2−}$ is the medium for the M−K cycle to occur. Furthermore, the NO activation performance as a part of the M−K mechanism is the main factor affecting CMRT catalyst activity. CMRT-350 displays the strongest NO activation performance and the highest low-temperature denitration activities. However, CMRT-250 is susceptible to NH$_3$ poisoning during the NH$_3$-SCR reaction and its Ru$_{\text{n+}}$ site has no catalytic effect; CMRT-450 has poor adsorption and activation capacity for NO and NH$_3$. These results demonstrate the significance of calcination temperature in preparing a highly effective NH$_3$-SCR catalyst.

**4. MATERIALS AND METHODS**

4.1. Catalyst Preparation. The CMRT mixed-oxide catalyst was synthesized using a wet co-impregnation method. Cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O), manganese nitrate (Mn(NO$_3$)$_2$), and ruthenium nitrosyl nitrate (N$_2$O$_{5}$Ru) were used as sources of cerium, manganese, and ruthenium, respectively, and anatase TiO$_2$ powder was used as a carrier. The specification and supplier information of the experimental materials are shown in Table S2. First, the weighed cerium nitrate hexahydrate, manganese nitrate, and ruthenium nitrosyl nitrate were dissolved in deionized water at room temperature and stirred vigorously for 5 min, followed by the slow addition of anatase TiO$_2$ powder to the active solution under 1 h continuous mixing. The mixed solution was maintained by vigorous stirring with a heat-collecting magnetic
stirrer at 60 °C until the solution evaporated to obtain a solid product, which was dried in an electrically heated drying oven at 110 °C overnight. The dried mixture was heated from room temperature at a heating rate of 5 °C/min within the air to the set temperatures that were 250, 300, 350, 400, and 450 °C accordingly. After calcination at the set temperature for 4 h, the mixture was naturally cooled to 200 °C. This catalyst is referred to as CMRT-X, where X represents the calcination temperature. The CMRT catalyst consists of 2.41 wt % Ce, referred to as CMRT-X, where X represents the calcination temperature.

4.2. Catalyst Characterization. The X-ray diffraction (XRD) patterns were measured by a Rigaku SmartLab (3 KW) (Japan) with Cu Kα radiation at 40 kV and 30 mA and collected at 2θ = 10–90° with a step size of 0.02°. The N2 adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020 M surface area and pore size analyzer at −196 °C. The specific surface areas were evaluated by the Brunauer–Emmett–Teller (BET) method. The scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy element distributions analysis were performed on a JSM-6490LV.

Hydrogen temperature-programmed reduction (H2-TPR) was performed by a ChemBem TPR/TPD automated chemisorption apparatus from Quantachrome. A total of 100 mg of the sample (40–60 mesh) was used and pretreated at 200 °C in a flow of Ar (60 mL/min) for 1 h and cooled all the way down to 50 °C. Then, the 10 vol % H2–Ar (60 mL/min) mixed gas was injected for 20 min. Last, the temperature was increased from 50 to 600 °C at 10 °C/min. The H2 consumption was measured by a thermal conductivity detector (TCD).

The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo ESCALAB 250XI with a monochromatized Al-Kα X-ray source (1486.6 eV) and a passing energy of 25 eV. The C 1s (binding energy 284.8 eV) of adventitious carbon was used as the reference. The Ce 3d peak, Mn 2p peak, Ru 3d peak, and O 1s peaks were deconvoluted by fitting Lorentzian and Gaussian functions (30%), and the half-height widths of the same peaks of the same elements in the five catalysts were fixed.

NH3-TPD was carried out on the Hiden HPR-20 EGA. A total of 100 mg of the sample (40–60 mesh) was used and pretreated at 200 °C in a flow of He (50 mL/min) for 1 h. After being cooled down to 47 °C, the sample was saturated with a flow of 2 vol % NH3/He (30 mL/min) for 1 h and was flushed by He (50 mL/min) for 1 h, and then TPD was run in He (50 mL/min) from 47 to 450 °C at 10 °C/min. The signal of desorbed NH3 species (m/z = 17) was recorded.

NO + O2-TPD was carried out on the Hiden Analytical QIC-20. A total of 100 mg of the sample (40–60 mesh) was pretreated in He (40 mL/min) at 200 °C for 1 h and cooled all the way down to 26 °C. Then, the sample was exposed to a flow of 550 ppm NO and 10 vol % O2/He (40 mL/min) for 1 h to succeed in saturated surface adsorption of NOx on the sample, followed by He (40 mL/min) purging for 1 h. Finally, the TPD test was carried out in a He flow (40 mL/min) from 26 to 500 °C. The signal of desorbed NO species (m/z = 30) and NO2 species (m/z = 46) was recorded.

The in situ DRIFT measurements were performed on a Thermo Fisher Nicolet iZ10 spectrometer with an MCT detector cooled by liquid nitrogen. Before every test run, the catalyst powders were pretreated with purified N2 (50 mL/min) in a sample crucible at 200 °C for 1 h and then absolutely cooled to the specified temperature. The background spectra were recorded at the corresponding temperature and mechanically deducted from the sample spectra. The subsequent reaction conditions were employed in DRIFT experiments: 550 ppm NH3/and/or 550 ppm NO + 10% O2, balance N2, and the total rate of flow was set as 50 mL/min. The spectrums were collected from 650 to 4000 cm−1 at a resolution of 4 cm−1 (number of scans = 32).

In the NH3 oxidation, 200 mg of the catalyst (40–60 mesh) was used. The reactant gas for the NH3 oxidation was composed of 550 ppm NH3 + 10% O2/balanced N2. Its total rate of flow was 100 mL/min, and the gas hourly space velocity (GHSV) was 23 000 h−1. The concentration of NO within the tail gas was detected by a flue gas analyzer (Testo 350, Germany). A thermogravimetric analysis (TGA) was conducted by a DTY-60H Thermal Analyzer (SHIMADZU-GL, Japan) to spot the decomposition of the precursor nitrate (Figure S6). The sample (approximately 8 mg) was heated from 30 to 600 °C at 10 °C/min with flowing air (50 mL/min).

4.3. Catalytic Activity Testing. The catalytic activities of the CMRT-X catalysts for NH3-SCR were investigated in a fixed-bed quartz reactor at atmospheric pressure. The catalyst (200 mg; 40–60 mesh) with the reactant gas was as follows: 550 ppm NO, 550 ppm NH3, 10% O2, 110 ppm SO2, and N2 in balance. The gas hourly space velocity was ~23 000 h−1. Moreover, NO, NO2, NH3, and O2 concentrations were detected by a flue gas analyzer (Testo 350; Testo SE & Co. KGaA, Germany), while N2O was monitored via a N2O analyzer. The catalyst bed was heated at 10 °C/min, and then the reaction temperature was stably maintained for 0.5 h. The NOx conversion and N2 selectivity of the catalysts were calculated according to the following formulas:

\[
\text{NO conversion(\%) } = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\% 
\]

\[
\text{N}_2 \text{ selectivity(\%)} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\%
\]

where 
[\text{NO}_x] = [\text{NO}] + [\text{NO}_2] \text{ and the [NO}_x]_{\text{in}} \text{ and [NO}_x]_{\text{out}}\text{ represent the inlet and outlet concentrations of NOx at the steady state, respectively. The } [\text{N}_2\text{O}]_{\text{out}} \text{ is the outlet concentration of } N_2O.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05194.

Further additional information about the N2 selectivity of CMRT-X catalysts; influence of SO2 on the NOx conversion of the CMRT-250, 350, and 450 catalysts; catalytic activities of CT, CRT, CMT, and CMRT catalysts calcined at 350 °C and anatase TiO2 powder for the NH3-SCR reaction; SEM and EDS mapping images of the CMRT-350 catalyst; area of Ru4+ in XPS; experimental materials; profiles of H2-TPR of all catalysts and H2-TPR note; and TGA profile of the CMRT-uncalcined catalyst (PDF).
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Notes
The authors declare no competing financial interest.

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DEDICATION

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