Effect of Indium Addition on the Low-Temperature Selective Catalytic Reduction of NO\textsubscript{x} by NH\textsubscript{3} over MnCeO\textsubscript{x} Catalysts: The Promotion Effect and Mechanism

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ABSTRACT: A MnCeInO\textsubscript{x} catalyst was prepared by a coprecipitation method for denitrification of NH\textsubscript{3}-SCR (selective catalytic reduction). The catalysts were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry, scanning electron microscopy, X-ray photoelectron spectroscopy, Brunauer−Emmett−Teller analysis, H\textsubscript{2} temperature-programmed reduction, and NH\textsubscript{3} temperature-programmed desorption. The NH\textsubscript{3}-SCR activity and H\textsubscript{2}O and SO\textsubscript{2} resistance of the catalysts were evaluated. The test results showed that the SCR and water resistance and sulfur resistance were good in the range of 125−225 °C. The calcination temperature of the Mn\textsubscript{6}Ce\textsubscript{0.3}In\textsubscript{0.7}O\textsubscript{x} catalyst preparation was studied. The crystallization of the Mn\textsubscript{6}Ce\textsubscript{0.3}In\textsubscript{0.7}O\textsubscript{x} catalyst was poor when calcined at 300 °C; however, the crystallization is excessive at a 500 °C calcination temperature. The influence of space velocity on the performance of the catalyst is great at 100−225 °C. FTIR test results showed that indium distribution on the surface of the catalyst reduced the content of sulfate on the surface, protected the acidic site of MnCe, and improved the sulfur resistance of the catalyst. The excellent performance of the Mn\textsubscript{6}Ce\textsubscript{0.3}In\textsubscript{0.7}O\textsubscript{x} catalyst may be due to its high content of Mn\textsuperscript{4+}, surface adsorbed oxygen species, high specific surface area, redox sites and acid sites on the surface, high turnover frequency, and low apparent activation energy.

HIGHLIGHTS

• A novel NH\textsubscript{3}-SCR catalyst was developed by doping indium into MnCeO\textsubscript{x}.
• The MnCeInO\textsubscript{x} catalyst showed >90% conversion of NO\textsubscript{x} at 125−225 °C.
• The resistance to H\textsubscript{2}O and SO\textsubscript{2} of the Mn\textsubscript{6}Ce\textsubscript{0.3}In\textsubscript{0.7}O\textsubscript{x} catalyst was enhanced significantly.
• The mechanism of catalysis of NH\textsubscript{3}-SCR of the novel catalyst was analyzed.
• The doping of indium improved the TOF value of the catalyst and reduced the apparent activation energy of the catalyst.

1. INTRODUCTION

NO\textsubscript{x} is a harmful pollutant produced by fossil fuels mainly from industrial processes and residential life. The natural degradation way is to combine it with water to produce nitric acid into the earth with rain. A large amount of nitric acid combined with rain will form acid rain, and gaseous NO\textsubscript{x} will form photochemical smog, which has a great impact on human health and ecological balance.\textsuperscript{1} In recent years, the government had higher and higher requirements for NO\textsubscript{x} emission standards of enterprises.\textsuperscript{7} Many denitrification technologies have been developed to meet the standards.\textsuperscript{3−5} At present, the vanadium catalyst (V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2}) is widely used in industry. Due to its strict high-temperature operating window (290−400 °C) and toxic pollution of vanadium sublimation at high temperatures, the working environment of the catalyst has many restrictions.\textsuperscript{6,7} With the improvement of waste heat utilization technology of flue gas in power plants, the requirement of flue gas denitrification for catalyst temperature is higher and higher. Therefore, the development of a low-temperature denitration catalyst with high efficiency is very promising.\textsuperscript{5,9} NH\textsubscript{3}-SCR (selective catalytic reduction) is an approach for effective NO\textsubscript{x} reduction.\textsuperscript{10} Therefore, it is very promising to develop catalysts suitable for low-temperature NH\textsubscript{3}-SCR technology instead of high-temperature active catalysts.

Among all the studied metals, MnO\textsubscript{x} is widely studied for its excellent low-temperature catalytic activity, but it cannot be applied in practice due to its poor water and sulfur resistance.\textsuperscript{11}
Other metal oxides have been added to further improve their low-temperature activity and stability. Because of its excellent redox performance, cerium was used as an enhancer to dope the original catalyst to improve the catalyst activity.\(^{12}\) Li et al. prepared Mn\(–\)CeO\(_x\) nanospheres using the geothermal approach with excellent denitration performance but only at low space velocity.\(^{13}\) Andreoli et al. prepared a MnO\(_x\)-CeO\(_x\) catalyst through the amino acetic acid method.\(^{14}\) Although it has an excellent conversion rate at 150–280 °C, its selectivity is poor. Although cerium has improved the sulfur resistance of the MnO\(_x\) catalyst, it still needs to be further improved.\(^{15–17}\) Decolatti et al. synthesized In-NH\(_4\)-zeolites and found that indium species could promote the oxidation of NO to NO\(_2\). The higher the indium content meant the better the denitrification effect.\(^{18}\) Pan et al. found that surface indium species can react with SO\(_2\) and H\(_2\)O to produce In\(_2\)(SO\(_4\))\(_3\).\(^{19}\) It was found that the low-temperature denitrification performance could be significantly improved by H\(_2\) treatment at 400 °C for 60 min, although the sulfate radical could not be completely removed.

In this work, the denitrification performance of MnCeO\(_x\) and MnCeInO\(_x\) catalysts with different ratios of In and the stability in the presence of water vapor and SO\(_2\) have been tested using an NH\(_3\)-SCR denitrification device at 100–275 °C. The gas hourly space velocity (GHSV) was 120,000 h\(^{-1}\). The catalysts were characterized by FTIR, SEM, XRD, BET, XPS, H\(_2\)-TPR, and NH\(_3\)-TPD. The possible reaction pathways were studied.

2. RESULTS AND DISCUSSION

2.1. Catalyst Performance Analysis. Figure 1 shows the NO\(_x\) conversion efficiency of MnCeO\(_x\) and a series of MnCeInO\(_x\) with different proportions. The T80 (NO\(_x\) conversion efficiency of >80%) of Mn\(_6\)CeO\(_x\) is at 125–200 °C. Figure 2 shows the water and sulfur resistance of Mn\(_6\)Ce\(_{0.3}\)In\(_{0.7}\)O\(_x\) and Mn\(_6\)CeO\(_x\) catalysts. (B) FTIR spectra of Mn\(_6\)Ce\(_{0.3}\)In\(_{0.7}\)O\(_x\) and Mn\(_6\)CeO\(_x\) catalysts treated in simulated flue gas at 150 °C for 60 min. Reaction conditions: 500 ppm NH\(_3\), 500 ppm NO, 5 vol % O\(_2\), 5 vol % H\(_2\)O, 100 ppm SO\(_2\), and balance N\(_2\) (GHSV = 120,000 h\(^{-1}\)).
calcination temperatures, which leads to the agglomeration of catalysts after calcination at 500 °C. Increasing the volume of the catalysts could increase the conversion efficiency of MnCeO$_x$. The calcination temperature of 400 °C has a great influence on the number of active sites and facilitates the processing of more feed gas. The calcination temperature has a great influence on the conversion efficiency of the catalyst. At 300 °C, the catalyst showed poor catalytic activity, the best conversion rate was only 90.8%, and T80 had a temperature operating window of 125−250 °C. When the calcination temperature is 500 °C, the conversion efficiency of the catalyst is slightly lower than the calcination temperature of 400 °C but its T90 still has a wide temperature operating window of 125−225 °C. It can be seen from the XRD diagram that the crystallization of the catalyst after calcination at 500 °C is higher than the other two calcination temperatures, which leads to the agglomeration of CeO$_2$ at the catalyst surface and the generation of more MnO$_y$, affecting the catalytic efficiency. XRD patterns at a calcination temperature of 300 °C showed wide and mixed peaks, indicating that the catalyst was poorly formed and not fully calcined.

Figure 2A shows the water and sulfur resistance test results of Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ and Mn$_6$CeO$_x$ catalysts at 150 °C. First of all, the catalyst was stably exposed to raw gas at 150 °C for 1 h, 5% H$_2$O was passed through the catalyst for continuous testing for 5 h, and then, the water vapor was closed. Then, 100 ppm SO$_2$ was passed one hour after catalyst recovery. SO$_2$ was closed after the continuous test for 5 h, and then, we waited for recovery for another hour. On this basis, 5% H$_2$O and 100 ppm SO$_2$ were added simultaneously, water vapor and SO$_2$ were closed after 5 h of monitoring, and the recovery of the catalytic efficiency was detected for 1 h.

In practical engineering applications, H$_2$O and SO$_2$ are the influencing factors that cannot be ignored. The sulfiziation of catalysts and the formation of NH$_4$HSO$_x$ are the key reasons leading to the reduction of catalytic efficiency of catalysts. In Figure 2A, the water resistance of the two catalysts is similar, and the conversion rate decreases by 8%. After H$_2$O is closed, Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ shows a stronger recovery ability than Mn$_6$CeO$_x$, and the conversion efficiency of Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ returns to the state before water is added. The Mn$_6$CeO$_x$ catalyst recovered 5%. When 100 ppm SO$_2$ was introduced, the catalytic efficiency of Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ suddenly dropped, which may be due to part of the active sites on the catalyst surface being covered by sulfide or ammonium sulfate when SO$_2$ was passed through the catalyst in the early stage. After 1 h of SO$_2$ induction, the catalytic efficiency recovered 91.6%, which was related to the decomposition of ammonium sulfate on the catalyst surface, releasing part of the active sites and causing the efficiency of the catalyst to rebound. Then, the conversion rate gradually decreased to 89.4% with the increase in time and recovered 93% after the closure of SO$_2$. The catalytic efficiency of Mn$_6$CeO$_x$ decreased gradually with the increase in time, decreased to 76% after 5 h, and recovered 81.5% after closing SO$_2$. When the water and sulfur resistance of the two catalysts was tested, Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ showed a better effect than Mn$_6$CeO$_x$. The conversion efficiency of Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ and Mn$_6$CeO$_x$ decreased to 82.4 and 67% after the 5 h test, respectively. The conversion efficiency of Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ and Mn$_6$CeO$_x$ recovered 87.2 and 70.7% after water vapor and SO$_2$ were closed, respectively. The addition of indium significantly improved the resistance ability of the Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ catalyst to H$_2$O and SO$_2$. According to the recovery ability of the Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ catalyst after the test of sulfur resistance, SO$_2$ had little effect on it, and the main effect was from water vapor. The influence on the recovery ability of the two catalysts through the H$_2$O and SO$_2$ resistance tests revealed that a part of the active site of the catalyst may be covered by (NH$_4$)$_2$SO$_4$ to obtain the difference of the surface structure of the catalysts after the water and sulfur resistance test, the catalysts were characterized by Fourier transform infrared spectroscopy (FTIR). Figure 2B shows the FTIR spectra of Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ and Mn$_6$CeO$_x$ catalysts after H$_2$O and SO$_2$ resistance tests. In FTIR tests of the Mn$_6$CeO$_x$ catalyst, 3414 cm$^{-1}$ was attributed to the vibration of the O−H bond of H$_2$O.23,24 In the FTIR test of the Mn$_6$Ce$_{0.3}$In$_{0.7}$O$_x$ catalyst, 3390 cm$^{-1}$ was attributed to the N−H tensile vibration mode of NH$_3$.24,25 According to literature reports, 3200 cm$^{-1}$ was attributed to the formation with other forms of NH$_3$ and NH$_4^+$.24 The 1631−1627 cm$^{-1}$ peak belongs to adsorbed NO$_2$.26 The 1450−1443 cm$^{-1}$ peak belongs to NH$_4^+$ formed by adsorption at the Bronsted acidic sites.27,28 The 1400−1383 cm$^{-1}$ peak was attributed to...
ammonium sulfate and 1114–1070 cm\(^{-1}\) to sulfate. The 1265 cm\(^{-1}\) peak was attributed to mononitric nitrite. The 863–862 cm\(^{-1}\) peak belongs to physical adsorption or weak phase adsorption of NH\(_3\). In the wavelength range of less than 800 cm\(^{-1}\), it belongs to the vibration between metal and oxygen atoms, and 558–569 cm\(^{-1}\) was related to the vibration of the Mn–O bond. By comparing the results of the two catalysts, the two catalysts both contain single-toothed nitrate, adsorbed NO\(_3\) adsorbed NH\(_3\), and NH\(_4^+\) but do not contain double-toothed nitrate. In addition, they all contain ammonium sulfate and sulfate. The results showed that SO\(_2\) inhibited the formation of nitrates on the Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O catalyst and had little effect on the adsorption of nitrates and ammonia on the monoxide. It is not difficult to see that the peak intensity of ammonium sulfate and sulfate on the Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O catalyst decreases obviously in the FTIR diagram, and the peak intensity increases in the range of 3000–3750 cm\(^{-1}\), which indicates that indium doping could effectively reduce the formation of ammonium sulfate and sulfate at the catalyst. Moreover, it can improve the chemisorption of NH\(_3\) and the formation of NH\(_4^+\).

2.2. XRD Analysis. Figure 3A presents the XRD results for the MnCeO\(_2\) and MnCeInO\(_3\) series. According to JADE 6 software, the MnCeO\(_2\) sample contains sharp XRD peaks of the MnO\(_2\) phase (PDF no. 89-5171) and the CeO\(_2\) phase (PDF no. 34-0394). The presence of MnO\(_2\), CeO\(_2\), In\(_2\)O\(_3\), and Mn\(_6\)O\(_3\) (PDF no. 24-0508) phases can be observed in the MnCeInO\(_3\) series. With the decrease in the cerium content and the increase in the indium content, the XRD peak of the CeO\(_2\) phase becomes weaker, and the peak strength of 37.2\(^\circ\) of the (100) crystal of MnO\(_2\) gets stronger. With the increase in the indium content, the (102) plane diffraction peak at 56.47\(^\circ\) of MnO\(_2\) decreases gradually, indicating that MnO\(_2\) exists as an amorphous component. The results indicated that indium was doped to inhibit the crystallization of CeO\(_2\) and promote the growth of the MnO(100) crystal. At the same time, the In\(_2\)O\(_3\) phase (PDF no. 22-0336) gradually appeared, indicating that the In\(_2\)O\(_3\) structure formed on the surface of MnCeO\(_2\).

In Figure 3B, the calcination temperatures of Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O\(_x\) catalysts were compared. The catalysts calcined at 300 °C have obvious diffraction peaks between 30 and 45° but no diffraction peaks in other ranges. It indicates that the catalyst is not fully formed. The catalyst calcined at 500 °C has an obvious diffraction peak of CeO\(_2\) at 2\(\theta\) = 28°, which indicates that the dispersed cerium can be condensed by calcination at high temperatures. At 2\(\theta\) = 33°, the Mn\(_2\)O\(_3\) crystal peak is formed, indicating that more Mn\(_2\)O\(_3\) is produced on the surface of the catalyst by calcination at high temperatures. The agglomeration of CeO\(_2\) and more Mn\(_2\)O\(_3\) negatively affects the performance of the catalyst. Combined with the denitration test results, studies showed that the catalyst calcined at 300 °C had the worst NO\(_x\) conversion, the efficiency was slightly better at 500 °C, and the efficiency was the best at 400 °C. In summary, the preparation temperature of Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O\(_x\) is between 2 and 20 nm, and the pore volume distribution is between 0 and 0.23 cm\(^3\)/g-nm. The

Figure 4. SEM morphology of (a–c) Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O\(_x\) and (d–f) MnCeO\(_2\) catalysts.

Figure 4c and Figure 4f, the particle diameter of the Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O\(_x\) catalyst is 7.5 μm, and the surface of the Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O\(_x\) catalyst is uneven and covered like microvilli. The particle diameter of the MnCeO\(_2\) catalyst is 12 μm, and the surface appears smooth and flat. The addition of indium changed the appearance and size of the MnCeO\(_2\) catalyst, which increased the specific surface area of the Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O\(_x\) catalyst.

2.4. Variation of the Specific Surface Area and the Pore Structure. Importantly, a larger specific surface area can provide more catalytic active sites and reaction paths for SCR catalytic reactions. The SEM results indicated that the morphology of the two catalysts also changed, so the difference between them was quantitatively studied by the N\(_2\) adsorption/desorption isothermal curve and pore size distribution. Figure 5 presents the nitrogen adsorption/desorption isotherm and pore size distribution of Mn\(_6\)Ce\(_0.3\)In\(_0.7\)O\(_x\) and MnCeO\(_2\) catalysts.
pore size and volume distributions of the Mn6CeOx catalyst are 3–18 nm and 0–0.15 cm³/g·nm, respectively. Table 1 lists the specific surface area, pore volume, and pore size of Mn6Ce0.3In0.7Ox and Mn6CeOx catalysts. Although the pore size of the catalyst decreases with indium doping, the specific surface area increases by 23.7%. The results are consistent with those of the hysteresis loop and SEM. Therefore, the doping of indium increases the pore volume of the catalyst, increases the surface area of the catalyst, and provides more catalytic active sites.

2.5. Analysis of Surface Element Valence States. In order to understand the properties of elements on the catalyst surface, XPS tests were carried out on Mn6Ce0.3In0.7Ox and Mn6CeOx catalysts, as shown in Figure 6. The Mn 2p, O 1s, Ce 3d, and In 3d spectra of the catalyst were fitted by XPSPEAK4.1. Figure 6A shows the deconvoluted peaks of Mn 2p for catalysts Mn6Ce0.3In0.7Ox and Mn6CeOx. The XPS spectra of the Mn 2p region showed a pair of peaks for all the samples, which were attributed to Mn 2p3/2 and Mn 2p1/2, denoted by "v" and "u" corresponding to the spin–orbit (642.0 eV), and Mn3+ (643.4–643.3 eV). Mn ions in Mn6Ce0.3In0.7Ox have a variety of valence states, which makes it easy to form a redox pair of Mn6+/Mn5+, causing a good NH3-SCR activity. The relative proportion of Mn6+ in the indium-doped Mn6Ce0.3In0.7Ox catalyst increased compared to Mn6CeOx (Table 2). Corresponding to the XRD results, the increase in the high valence state of Mn enhances the oxidation capacity of the Mn6Ce0.3In0.7Ox catalyst, thus improving the SCR performance.

Figure 6B shows the deconvoluted XPS spectra of O 1s in Mn6CeOx and Mn6Ce0.3In0.7Ox catalysts. The peak at 529.49 eV corresponds to the lattice oxygen O2−(Oβ). The peaks at 530.5–531.3 eV correspond to surface oxygen (Oα), such as groups belonging to defective oxides and hydroxyl oxygen (e.g., O2− or O−). Since Oα is more reactive and migrates more easily than Oβ, it could contribute to the oxidation of NO to NO2 in the SCR reaction, allowing the catalyst to exhibit a better performance in the oxidation reaction. The calculated Oα ratio of the Mn6Ce0.3In0.7Ox catalyst is shown in Table 2. The surface oxygen Oα content of the Mn6Ce0.3In0.7Ox catalyst (54.71%) is higher than that of Mn6CeOx (47.17%), indicating that the Mn6Ce0.3In0.7Ox catalyst has more surface oxygen Oα than the Mn6CeOx catalyst, which is beneficial for fast SCR reactions (4NH3 + 2NO + 2NO2 → 4 N2 + 6H2O) at low temperatures.

Figure 6C shows the fitting spectrum of Ce 3d. The XPS spectra of the Ce 3d region showed a pair of peaks for all the samples, which were attributed to Ce 3d5/2 and Ce 3d3/2, denoted by "u" and "v" corresponding to the spin–orbit.
component of Ce 3d_{5/2} and Ce 3d_{3/2}, respectively. It can be observed that there are 8 peaks of u, u1, u2, v, v1, v2, and v3 for Ce 3d where v1 and u3 are Ce^{3+} and the other peaks are Ce^{4+}. On the whole, the cerium element in the two catalysts mainly exists in the form of Ce^{4+} ions, and only a small amount of Ce^{3+} exists. In Table 2, the Ce^{3+}/Ce ratios of Mn_{6}Ce_{0.3}In_{0.7}O_{x} and Mn_{6}CeO_{x} catalysts are 21.1 and 18.3%, respectively. It indicates that the doping of indium leads to the decrease in the relative content of Ce^{4+}, which is because the In^{3+} ions inserted into the catalyst replace the position of Ce^{4+}, thus changing the oxygen content in the sintering process of the catalyst, transforming Ce^{4+} into Ce^{3+}. Increasing the concentration of Ce^{3+} at the catalyst surface can promote the formation of charge imbalance, unsaturated bonds, and vacancies. Therefore, the following processes may occur between Ce^{4+} and Ce^{3+} on the catalyst surface in the SCR reaction: (1) 2CeO_{2} → Ce_{2}O_{3} + O^{2−} and (2) Ce_{2}O_{3} + 1/2O_{2} → 2CeO_{2}. In this process, the oxygen in the flue gas is adsorbed and dissociated on the catalyst surface through the oxygen vacancy to produce oxygen with high fluidity and promote the oxidation of NO to NO2.

Figure 6D shows the deconvolution of the In 3d_{5/2} signal, and two peaks can be obtained, namely, a binding energy of 444.34 eV (structure related to InO_{x} species) and a binding energy of 444.91 eV (structure similar to InO^{+} species). Surface (InO)^{+} is considered to be the active site in the SCR reaction. The active site can bind to gaseous NH_{3} to form adsorbed ammonia and then dissociate NH_{3} to form −NH_{2} and [In(OH)]^{+}−, and the formation of these groups contributes to the fast SCR reaction.

2.6. Redox Property. The redox capacity of the catalyst was characterized by H_{2} temperature-programmed reduction (H_{2}-TPR). It is shown in Figure 7. After the split peak, it was observed that there are four reduction peaks for Mn_{6}CeO_{x} and Mn_{6}Ce_{0.3}In_{0.7}O_{x} catalysts. By comparing the H_{2} reduction curves of the two catalysts, the peaks of Mn_{6}CeO_{x} in the range of 100–300 °C can be divided into three peaks centered at 243, 265, and 394 °C. These three reduction peaks correspond to the reduction of MnO_{2} to nonstoichiometric dispersed MnO_{x} (1.5 < x < 2). At this point, the exposed high flow of oxygen on the catalyst surface was removed. MnO_{2} is then reduced to Mn_{2}O_{3}, at which time part of the lattice oxygen on the catalyst surface decreases. Finally, Mn_{3}O_{4} is reduced to Mn_{3}O_{4} and further to MnO. Chen et al. reported that the surface Ce^{4+} to Ce^{3+} reduction process also occurred at 394 °C. A very low and flat peak was observed at the center of 735 °C. According to the literature, the peak in the range of temperature more than 700 °C corresponds to the reduction of the surface and bulk of cerium oxide.

Compared with the Mn_{6}CeO_{x} catalyst, the Mn_{6}Ce_{0.3}In_{0.7}O_{x} catalyst exhibited a similar reduction peak in the temperature range of less than 400 °C. However, the peak values of these reduction peaks all shifted to the direction of low temperatures. The results indicate that the surface of the Mn_{6}CeO_{x} catalyst doped with indium is more prone to electron transfer, indicating that the catalyst has a lower SCR activity temperature, thus improving the catalytic performance. Peaks greater than 700 °C were not observed, possibly due to a decrease in the cerium content. There was no reduction peak, or the reduction peak moved to a higher-temperature region, which to some extent reduced the oxidation of cerium in the catalyst, inhibited the formation of nitrous oxide, and reduced the nonselective catalytic oxidation of NH_{x}. This may be one of the reasons for increased N_{2} selectivity. It can be seen that a new reduction peak is added at 458 °C, which is considered to be the indium phase prone to surface reduction, such as (InO)^{+} and InO_{y}^{+}, as shown in the following formula:

\[ \text{InO}^{+} + x\text{H}_{2} + y\text{H}^{+}\text{M}^{-} \rightarrow x\text{In}^{+}\text{M} + y\text{H}_{2}\text{O} \]  
\[ (\text{InO})^{+} + \text{H}_{2} \rightarrow \text{In}^{+} + \text{H}_{2}\text{O} \]

After indium doping, indium enters into the lattice of MnO_{2}, and the interaction between the components of the catalyst promotes the reduction of manganese and indium ions, improving the catalytic performance of the SCR catalyst. The reported H_{2} unit consumption of the catalyst Mn_{6}CeO_{x} (7.41 μmol·g\(^{-1}\)) was less than that of Mn_{6}Ce_{0.3}In_{0.7}O_{x} (8.62 μmol·g\(^{-1}\)). The results showed that the reduction peak positions of the two catalysts were not significantly different, but the reduction peaks shifted to low temperatures, indicating that indium doping improved the reduction properties of the Mn–Ce oxides to some extent, which was beneficial to the denitrification performance of the catalyst.

2.7. Acidity of the Catalysts. The acidity of Mn_{6}CeO_{x} and Mn_{6}Ce_{0.3}In_{0.7}O_{x} catalysts was studied by NH_{3}-TPD experiments, as shown in Figure 8. The amount and intensity of acid sites at the catalyst surface and the activation of NH_{3} at the catalyst surface were measured by the NH_{3}-TPD technique. In the temperature range of 50–800 °C, Origin 2021 software Gaussian fitting was used to obtain six analytical
peaks for catalysts Mn₆CeO₄ and Mn₆CeₐInₐO₇O₈. These peaks consisted of peak 1 (100 and 106 °C), peak 2 (147 and 145 °C), peak 3 (230 and 223 °C), peak 4 (442 and 458 °C), peak 5 (525 and 492 °C), and peak 6 (580 and 548 °C). According to literature reports, below 350 °C peak 5 (525 and 492 °C) and peak 6 (580 and 548 °C) are caused by the adsorption of NH₃ at the Brønsted or Lewis acid sites. It is well-known that the desorption peak position and the desorption peak area of a catalyst correspond to the strength and quantity of the acid, respectively.59,60 The amount of surface acid sites of Mn₆CeO₄ and Mn₆CeₐInₐO₇O₈ catalysts can be estimated after integrating the NH₃-TPD curves. The integral area shown in Figure 8 indicated that the acid content of the Mn₆CeO₄ catalyst was 18.7 μmol·g⁻¹, which was less than that of the Mn₆CeₐInₐO₇O₈ catalyst (19.3 μmol·g⁻¹). The results showed that the doping of indium in Mn₆CeO₄ catalysts could improve the number of surface acid sites and enhance the adsorption of NH₃ on the catalysts to a certain extent.

2.8. Kinetic Study. Arrhenius plots of Mn₆CeₐInₐO₇O₈ and Mn₆CeO₄ catalysts in the range of 110−140 °C are shown in Figure 9A. The turnover frequency (TOF) of Mn₆CeₐInₐO₇O₈ and Mn₆CeO₄ catalysts in the range of 100−220 °C is shown in Figure 9B. The test method was to fully mix 0.01 g of the catalyst and 0.09 g of SiO₂ for testing in an NH₃-SCR evaluation device to ensure that the reactivity was not a physical or weak chemical adsorption of NH₃ and NH₄⁺ produced by the combination of NH₃ and surface hydroxyl groups. Peaks 4, 5, and 6 belong to medium-strong acid sites and are caused by the adsorption of NH₃ at the Brønsted or Lewis acid sites. It is well-known that the desorption peak position and the desorption peak area of a catalyst correspond to the strength and quantity of the acid, respectively.59,60 The amount of surface acid sites of Mn₆CeO₄ and Mn₆CeₐInₐO₇O₈ catalysts can be estimated after integrating the NH₃-TPD curves. The integral area shown in Figure 8 indicated that the acid content of the Mn₆CeO₄ catalyst was 18.7 μmol·g⁻¹, which was less than that of the Mn₆CeₐInₐO₇O₈ catalyst (19.3 μmol·g⁻¹). The results showed that the doping of indium in Mn₆CeO₄ catalysts could improve the number of surface acid sites and enhance the adsorption of NH₃ on the catalysts to a certain extent.

2.9. Discussion. The results show that the MnCeOₓ catalyst has a temperature operating window of T80 of 125−200 °C at GHSV = 120,000 h⁻¹ and shows good activity but poor activity in other temperature test sections. The activation of the MnCeOₓ catalyst was promoted by adding indium. For example, the temperature window of the catalyst T90 increases from 150−175 to 125−225 °C. The activation energy of the Mn₆CeₐInₐO₇O₈ catalyst is lower than that of the Mn₆CeO₄ catalyst obtained from the Arrhenius plot (Figure 10A) results.
helpful to improve the activity of the catalyst. In the XRD results of different calcination temperatures, it can be found that the crystallization of the catalyst calcined at 300 °C was bad. The crystallization of the 400 °C calcined catalyst was excessive. The results showed that the crystallinity of the catalyst had a significant effect on the catalytic activity. It can be seen from the SEM images and specific surface area and pore size test results that the doping of indium changes the morphology and size of catalyst particles, increases the specific surface area and pore capacity of the catalyst, and thus provides more surface active sites. XPS characterization was conducted to understand the surface element valence, surface oxygen state, acidity, and reducibility of the catalyst and then speculate the catalytic process of the catalytic reaction. The XPS test results show that the Mn6Ce0.3In0.7Ox catalyst has a higher proportion of Mn4+ and surface oxygen (Ox) than the Mn6CeO3 catalyst, which improves the catalytic oxide behavior and improves the SCR performance. In the Mn6Ce0.3In0.7Ox catalyst, the In3+ ions replace the position of Ce4+, resulting in the relative increase in the Ce3+ content and surface oxygen defects.45 This oxygen vacancy can make the oxygen in the flue gas adsorbed and dissociated over the catalyst surface to produce oxygen with high flow and promote the oxidation of NO to NO2. In the reduction test, the reduction peak temperature of the Mn6Ce0.3In0.7Ox catalyst was reduced, indicating that the SCR activity temperature of the Mn6Ce0.3In0.7Ox catalyst was reduced, which is consistent with the calculation of the apparent activation energy. At around 700 °C, the hydrogen reduction curve of the Mn6Ce0.3In0.7Ox catalyst did not show the reduction peak of cerium, indicating that the oxidation of the catalyst was reduced to some extent and the N2O production was inhibited. In the test of surface acidity, the Mn6Ce0.3In0.7Ox catalyst showed enhanced surface acid site intensity and increased adsorption capacity for NH3, indicating that more NH3 was activated or decomposed on its surface and then reacted with adsorbed NH4+ at Bronsted acid sites to produce intermediate products NH2NO and NH4NO2. NH2NO and NH4NO2 were further decomposed into nitrogen and water due to instability, and NH4NO3 will further combine with NO to generate NH2NO2 and NO2 at low temperatures. As the temperature increases, NH2NO2 will decompose into H2O and harmful gas N2O. The possible reaction process on the surface of the Mn6Ce0.3In0.7Ox catalyst is given by the following:

\[
\text{InO + NH}_3(g) \rightarrow \text{InOH + NH}_4(ad) \quad (8)
\]

\[
\text{InOH + NH}_3(g) \rightarrow \text{In - O - NH}_4(ad) \quad (9)
\]

\[
\text{MnO}_x + O_x(g) \rightarrow \text{MnO}_x + 20(ad)(1.5 < x < 2) \quad (10)
\]

\[
\text{CeO}_x + O_x(g) \rightarrow \text{CeO}_x + 20(ad)(1.5 < x < 2) \quad (11)
\]

\[
2\text{NO(g) + O}_2(g) \rightarrow 2\text{NO}_2(g) \quad (12)
\]

\[
\text{NO(g) + O(ad) \rightarrow NO}_x(ad) \quad (13)
\]

\[
\text{NO}_2(g) + O(ad) \rightarrow \text{NO}_x(ad) \quad (14)
\]

\[
\text{NH}_3(ad) + \text{NO(g)} \rightarrow \text{NH}_3\text{NO(ad)} \rightarrow \text{N}_2(g) + \text{H}_2\text{O(g)} \quad (15)
\]

\[
\text{NH}_4(ad) + \text{NO}_x(ad) \rightarrow \text{NH}_4\text{NO}_x(ad) \quad (16)
\]

\[
\text{NH}_4(ad) + \text{NO}_x(g) \rightarrow \text{NH}_4\text{NO}_x(ad) \quad (17)
\]

\[
\text{NH}_2(ad) + \text{NO}_x(g) \rightarrow \text{NH}_2\text{NO}_x(ad) \rightarrow \text{N}_2(g) + \text{H}_2\text{O(g)} \quad (18)
\]

\[
\text{NH}_4(ad) + \text{NO}_x(ad) \rightarrow \text{NH}_4\text{NO}_x(ad) + \text{NO}_x(g) \quad (19)
\]

\[
\text{NH}_4(ad) + \text{NO}_x(ad) \rightarrow \text{NH}_4\text{NO}_x(ad) \quad (20)
\]

\[
\text{NH}_4\text{NO}_x(ad) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O(g)} \quad (21)
\]

\[
\text{NH}_4\text{NO}_x(ad) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O(g)} \quad (22)
\]

\[
2\text{InOH} + \text{O(ad)} \rightarrow \text{InO} + \text{H}_2\text{O(g)} \quad (23)
\]

3. CONCLUSIONS

MnCeInOx catalysts were prepared for NH3-SCR by a coprecipitation method. The test results showed that Mn6Ce0.3In0.7Ox exhibited the best catalytic activity at low temperatures, and its optimal preparation temperature was 400 °C. The temperature window for denitrification efficiency greater than 90% (T90) was extended from 150–175 to 125–225 °C. The Mn6Ce0.3In0.7Ox catalyst had a low apparent activation energy (Ea) and a high turnover frequency (TOF) compared to the undoped catalyst without indium, indicating that the doping of indium improved the synergistic effect of the catalyst active sites. In addition, indium doping reduced the formation of sulfate on the catalyst and enhanced the water and sulfur resistance of the Mn6CeO3 catalyst. The denitrification efficiency of the Mn6Ce0.3In0.7Ox catalyst was higher than that of Mn6CeO3 by 15.4% after a 5 h test in the presence of 5% H2O and 100 ppm SO2 in the feed gas. The enhanced redox performance and NH3 adsorption capacity of the Mn6Ce0.3In0.7Ox catalyst are related to the increase in the specific surface area of the catalyst and the increase in the ratio of Mn4+ ions and surface oxygen (Ox) on the surface.
4. EXPERIMENTAL SECTION

4.1. Catalysis Preparation. All samples were synthesized by coprecipitation. First, the MnCeO₃ catalyst was synthesized, in which Mn:Ce = 6:1 (molar ratio). Next, a series of MnCeInOₓ catalysts were prepared, in which Mn:(Ce + In) = 6:1 and Ce:In = 9:1, 7:3, 5:5, 3:7, and 1:9 (molar ratio). First, Mn(CH₃COO)₂·4H₂O, In(NO₃)₃·H₂O, and Ce(NO₃)₃·H₂O were added one by one to 100 mL of distilled water at a water bath at 30 °C and stirred until a clear solution. An equal stoichiometric ratio of (NH₄)₂CO₃ was dispersed in 10 mL of deionized water. It was then added into the clear salt solution. After continuous vigorous stirring, the mixture was adjusted to a pH value between 9 and 10 using 4 M NaOH solution and then covered with a cling film to be sealed, and the mixture was continued to be stirred for 2 h. Then, the suspension was allowed to stand at around 24 h at room temperature. The sediment was washed to pH = 7 using deionized water; then, the solid obtained was dried in a blast drying oven at 110 °C for 4 h. The prepared catalysts were named as MnₓCeᵧ(Inₐ)Oₙ (a + b = 1), MnₓCeO₃ was prepared by a similar approach without the inclusion of indium.

4.2. Catalyst Characterization and Computational Details. X-ray diffractometry (XRD) analysis for the samples was performed using a SmartLab (9 kW) rotating-target X-ray diffractometer of Keshikoshi Corporation (Japan).

In the Brunauer–Emmett–Teller (BET) test, the samples were pretreated by degassing at 180 °C and 5 mTorr under vacuum at a steady state. They were then tested at −196 °C using a Quantachrome Instruments Quadrasorb EVO. The catalyst morphology was observed by field emission scanning electron microscopy (FE-SEM) on a 15 kV Merlin compact device made by Carl Zeiss NTS GmbH (Germany).

The X-ray photoelectron spectra (XPS) of the samples were documented on a Thermo Fisher ESCALAB 250Xi spectrometer using monochromatic Al Kα as the X-ray source, calibrated with the C 1s peak of indeterminate carbon (binding energy of 284.8 eV). The splitting calculations of the Mn 2p energy of 284.8 eV). The splitting calculations of the Mn 2p was determined using monochromatic Al Kα as the X-ray source, calibrated with the C 1s peak of indeterminate carbon (binding energy of 284.8 eV). The splitting calculations of the Mn 2p energy of 284.8 eV). The splitting calculations of the Mn 2p.

For the samples, with Shirley as the background and the convolution Gaussian/Lorentzian ratio set to 80/20.

Temperature-programmed desorption (NH₃-TPD) of adsorbed NH₃ on the catalyst was carried out on an AUTO Chem II 2920 device (American Microelectronics Instruments, Inc.) equipped with a thermal conductivity detector (TCD). A 0.12 g sample was loaded into a quartz TPD reactor and pretreated in a 50 mL/min stream of N₂ and at 400 °C for 4 h. After being cooled to 50 °C, it was then purged with 10% NH₃/N₂ at a flow rate of 50 mL/min for 1 h to ensure complete saturation of the adsorption sites. The catalyst was then flushed with N₂ at the same gas flux for 1 h to take out the weakly sorbed NH₃. Then, the catalyst was heated from 50 to 800 °C with a constant N₂ flow rate with a ramp rate of 10 °C/min for NH₃ desorption, and the change in the NH₃ content during the process was detected in real time using a TCD detector.

Hydrogen temperature-programmed reduction (H₂-TPR) studies of mixed oxides were performed on an AUTO Chem II 2920 apparatus (American Microelectronics Instruments, Inc.) to determine their redox behavior. To perform these studies, a 0.12 g sample of the catalyst was put in a quartz U-shaped reaction cell. After the same sample pretreatment in pure argon as for NH₃-TPD studies, they were cooled to 50 °C in a stream of argon. The TCD signals were recorded in the temperature range of 50–800 °C with a 5% H₂/Ar mixture gas stream at a flow rate of 30 mL/min and a heating rate of 10 °C/min.

The surface adsorption of the catalyst was investigated by FTIR (Thermo Fisher) after the NH₃-SCR reaction and water and sulfur resistance tests.

4.3. Catalytic Performance Test. The schematic diagram of experimental equipment is shown in Figure 10. The catalytic activity of MnₓCeO₃ and MnₓCeₐ(Inₐ)Oₙ (a + b = 1) for NH₃-SCR in excess oxygen was studied in a vertical tubular furnace with a high-temperature-resistant quartz glass tube of 6 mm inner diameter, and the catalyst was placed in the heating section of the tubular furnace. Catalysts (40–60 mesh) (0.2 g) with a volume of about 0.25 mL were used. The reaction gas consists of 500 ppm NO, 500 ppm NH₃, 5% O₂, 100 ppm SO₂ (if used), 5% H₂O (if used), and balance N₂. The space velocity (GHSV) was about 120,000 h⁻¹. The concentration of NOx was measured by an electrochemical gas analyzer (Cairn-May Quintox Flue Gas Analyzer). The NOx conversion and N₂ selectivity were calculated using eqs 1 and 2, respectively:

\[ \text{NO}_x \text{ conversion} = \left(1 - \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \right) \times 100\% \]

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

The corner mark in represents the concentration of a substance in the raw gas. The corner mark out represents the concentration of a substance after catalyst treatment. Turnover frequency (TOF) values were calculated according to the following equation:

\[ \text{TOF} = \frac{\nu \times \alpha}{V_{\text{in}} \times \eta} \]

where \( \nu \) is the flow rate of nitrogen oxide (m³·s⁻¹), \( \alpha \) is the conversion of nitrogen oxide (%), \( V_{\text{in}} \) is the gas molar volume (m³·mol⁻¹), \( \eta \) is the number of moles of surface acidic sites (mol). The TOF values based on the surface acidic sites were estimated by NH₃-TPD.

The SCR kinetic parameters were calculated by the following equation:

\[ k = \frac{F}{W} \ln(1 - x) \]

where \( k \) is the reaction rate constant (cm³·g⁻¹·s⁻¹), \( F \) is the total flow rate (cm³·s⁻¹), \( W \) is the mass of the catalyst (g), and \( x \) is the NOx conversion.

Furthermore, the apparent activation energies (Ea) was calculated using the Arrhenius equation shown as follows:

\[ k = Ae^{-Ea/RT} \]
Experimental Research for the Simultaneous Removal of NO and SO₂

D. Gardiner, W. C., Jr. Reactions of sodium species in the promoted.

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Notes

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